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# FINAL TECHNICAL REPORT
## VOLUME II
## OPTICAL AND INFRARED PROPERTIES OF $Al_2O_3$ AT ELEVATED TEMPERATURES

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# FINAL TECHNICAL REPORT
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# OPTICAL AND INFRARED PROPERTIES OF $Al_2O_3$ AT ELEVATED TEMPERATURES

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| Reporting Period: | 1 August 1963 - 31 May 1964 |
| Prepared for: | Advanced Research Projects Agency<br>Washington, D.C. |
| Under Contract: | NOnr 3606(00) Amendment No. 2<br>ARPA Order No. 237/11-7-62 |
| Prepared by: | D. A. Gryvnak and D. E. Burch |
| Approved by: | M. H. Johnson, Director<br>Physics Laboratory |
| Project Manager: | D. J. Carlson<br>714-675-5100 Ext. 1573 |

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|---|---|
| Project Code No: | 3740 |
| Contract Date: | 15 October 1961 |
| Contract Amount: | $104,911 |
| Contract Expiration Date: | 31 May 1964 |

# ACKNOWLEDGMENT

The authors are pleased to acknowledge the assistance of Francis J. Gates in various phases of the experimental portion of this investigation.

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# SECTION 1

# INTRODUCTION AND SUMMARY

Particles of $Al_2O_3$ occur in many different types of flames, including those from solid propellant rockets, and it is important to know the contribution of these particles in order to understand the emissive properties of the flames. Bauer[1] and Plass[2] have used Mie theory to calculate the scattering cross-section, absorption cross-section and extinction coefficient of $Al_2O_3$ particles for different size distributions as a function of wavelength. Bauer has also discussed the dependence of the emissivity of "cloud" particles on these parameters. In order to make such calculations one must know with reasonable accuracy the values of the index of refraction n and the absorption coefficient k, which is directly related to the complex index of refraction, for the temperatures and wavelengths being considered. These authors both found that there was much to be desired in the way of experimental measurements of these quantities at the temperatures and wavelengths of interest. The index of refraction is known with very good accuracy throughout the region from the ultra-violet to about 5.5μ at temperatures only a few degrees different from room temperature. However, as far as is known by the authors no measurements have been made at temperatures even close to those occurring in flames.

Several workers[3-7] have measured either the transmittance or the absorption coefficient of $Al_2O_3$ as a function of wavelength at different temperatures as high as 1500°C. Some of these workers were interested in the properties of sapphire as a window material and, therefore, did not attempt to get accurate values of the absorption coefficient at wavelengths where it was so small as to be unimportant in determining the transmission. Others were interested in the transfer of energy by radiation and also did not try to measure small values of the absorption coefficient. The results of the different workers show quite a bit of inconsistency, particularly in the region from the visible to about 3.5μ where the absorption coefficient is so small that it is difficult to measure with good accuracy because of errors which arise from improperly accounting for the reflection losses or for scattered light. All of the experimental results which were available indicated a quite significant increase in the absorption coefficient with temperature; therefore, it seemed impractical to use values which were obtained at temperatures of 1500°C or less in calculating the emissivity in flames in the neighborhood of 2000°C.

Because of the apparent need for new information about the absorption coefficient and the index refraction as a function of both wavelength and temperature, the present investigation was undertaken. Samples of single crystals of $Al_2O_3$ (sapphire) were heated in a furnace to various temperatures up to 1700°C. The absorption coefficient and index of refraction were measured as a function of wavelength from 0.546μ to approximately 6μ. The index of refraction was found to increase only slightly with temperature but quite marked increases in the absorption coefficient were observed as the temperature was increased. The absorption coefficient was found to have a minimum in the neighborhood between 2 and 3μ and to increase to a value a couple of orders of magnitude higher at approximately 6μ.

Flames formed by burning $H_2$ and $O_2$ were used to heat the samples to even higher temperatures. At about 2020°C the absorption coefficient was found to be greater than the lower temperatures, except possibly in the region below about 1.5μ. As the temperature was increased further, a sudden increase in the emissivity was observed as the material became molten. The results indicate a discontinuous increase in absorption coefficient as one passes from the solid to the liquid state that is probably equal to a factor of about 30 or 40, and is possibly even greater throughout the wavelength region from the visible to about 4μ.

Measurements of the emission of polycrystalline $Al_2O_3$, which is a ceramic material made for use in high temperature furnaces, indicates that the general behavior of the emissivity is similar to what one would expect on the basis of the measurements of the absorption coefficient of the single crystal sapphire.

No attempts have been made to provide a theoretical explanation of the variations in absorption coefficient or index of refraction with wavelength or temperature.

# SECTION 2

# EXPERIMENTAL

## 2.1 INTRODUCTION

Two methods of heating sapphire samples which are referred to as the "furnace method" and the "flame method" were used in this investigation. An electrical furnace with molybdenum heater elements was used for temperatures as high as 1700°C. Furnace temperatures could be easily controlled and measured to within a few degrees C by the use of several thermocouples located throughout the furnace.

The flame method which used torches burning $H_2$ in $O_2$, enabled one to heat the samples to still higher temperatures, even to the point where one melted small portions of the samples. However, this flame method has the disadvantages that the temperature could not be controlled as well or measured as accurately as in the furnace. The temperature gradients and uncertainties in the temperature are discussed below in Sections 2.3, 3.1 and 3.2. $H_2$ rather than $CH_4$ or some other hydrocarbon was used as a fuel in order to avoid emission and absorption by carbon particles within the flame. Since the $H_2O$ formed by the combustion has strong emission bands near 1.4, 1.9, 2.7, and 6.3 microns, emission measurements of the sample were not made near these regions. Each of the heating methods are discussed below in Sections 2.2 and 2.3.

## 2.2 FURNACE METHOD

Figure 1 shows an optical diagram of the apparatus used in the furnace method. Radiation from either a Nernst glower or a tungsten filament passed a 13 c.p.s. chopper and was focussed on a set of slits

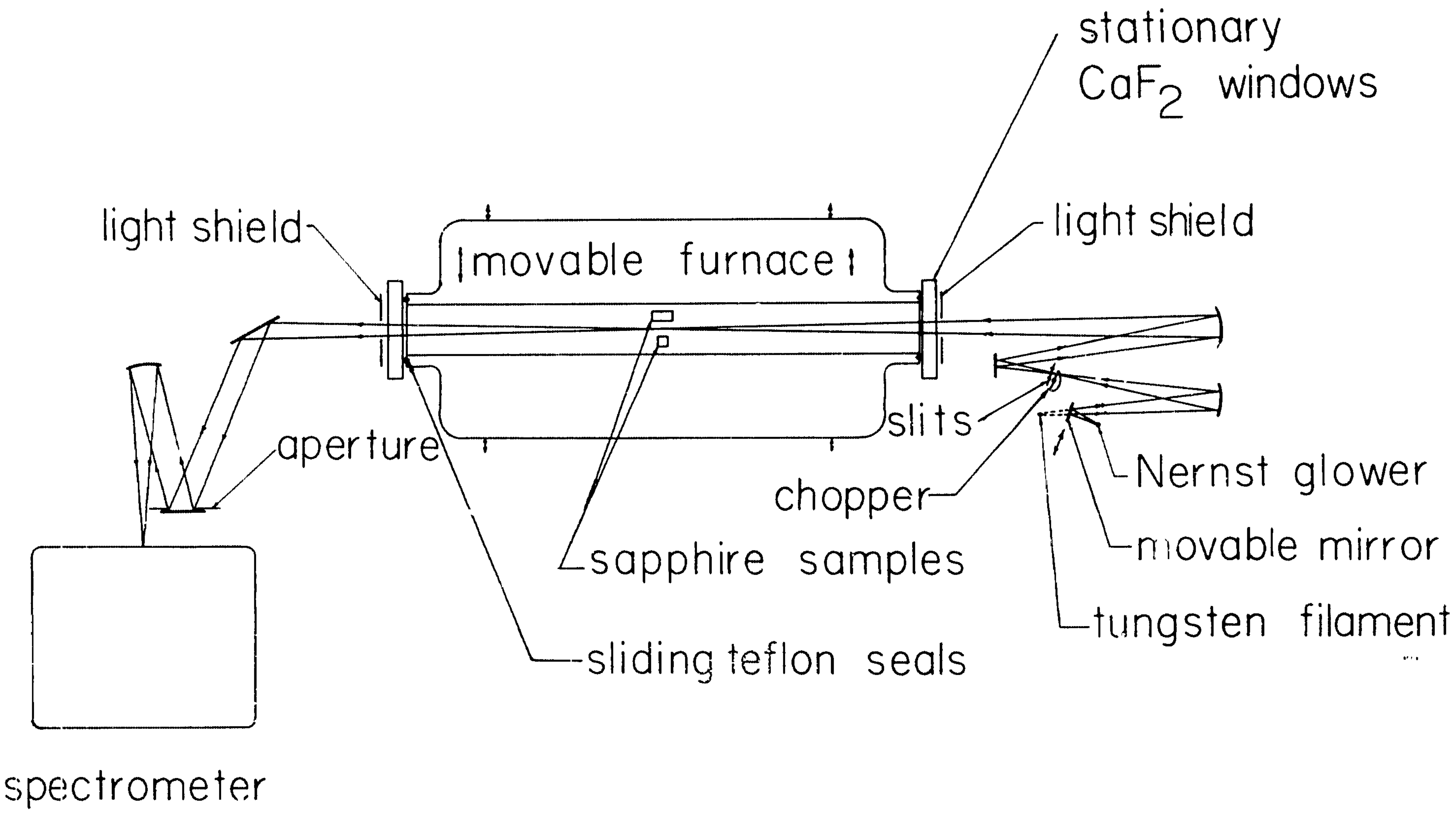

FIGURE 2-1 OPTICAL DIAGRAM OF APPARATUS USED TO STUDY SAMPLES HEATED WITH A FURNACE
The transmittance of two sapphire samples of different lengths were measured. The furnace and samples could be moved perpendicular to the beam to cause it to pass through either of the samples or between them.

whose height and width could be adjusted. Light going through the slits was then focussed near the center of the furnace and passed on forming an image on the slits of the spectrometer. The Nernst glower was used as a source for wavelengths greater than about 2μ while a tungsten filament was used for shorter wavelengths. In order to change from one source to another, the movable flat mirror near the source was moved to the desired position.

The figure shows the beam of radiation passing between the two sapphire samples which are located near the center of the furnace and have their optic axes parallel to the light beam. The furnace was mounted on a track so that it could be moved in a horizontal direction perpendicular to the light beam in order to cause the beam to go either between the samples or through either of them. The samples were held in a small tray about 10 cm long which was made by cutting a piece of ceramic $Al_2O_3$ tubing axially. The tubing had an O.D. of approximately 35 mm and was partially filled with a paste of $Al_2O_3$ in water with grooves formed to fit the samples. After drying for a few hours, the paste provided a rigid support for the samples.

The light beam from the source was chopped causing an AC signal on the detectors. The signal was then amplified, demodulated and displayed on a strip chart recorder. Since the detector electronics was sensitive only to a modulated signal with the same frequency as the chopper and with the proper phase, the radiation emitted by the furnace was not detected. A thermocouple was used as a detector for wavelengths $\lambda > 1\mu$, and a photomultiplier for shorter wavelengths. Only a few seconds were required to switch from one detector to the other.

In order to determine values of the absorption coefficient $k(\lambda)$ and the index of refraction n at any given wavelength $\lambda$, the signals observed by passing the beam through each of the two crystals and between them were compared. The method of comparison is discussed further below. Since the quantities being measured depend on a comparison of the three measurements, considerable care was necessary in order to avoid false answers resulting from improper spectral alignment. Each of the three signals must be measured with good accuracy in order that the quantities calculated from a difference between them will not contain large errors.

The purpose of the slits near the chopper was to limit the size of the image falling on the samples so that the image was small compared to the diameter, 12 mm, of the samples. This was done in order to avoid extraneous light which might be internally reflected from the sides of the samples. The image formed on the samples was approximately 2 mm x 2 mm; this was then re-imaged on the slit of the spectrometer with a reduction in size of about 3:1. The angle of divergence of the beam was limited by the diameter, 4 cm, of the opening in the end of the furnace and was actually less than is indicated in the drawing with an effective F ratio of approximately F/80.

The sapphire samples, which were rods 12 mm in diameter and whose lengths were 2.18, 3.38, 6.33, 12.9 and 25.4 mm, were obtained from Linde; and the ends were polished flat to 1/2 wavelength of green light with the faces parallel to a few seconds of arc; and the optics axis parallel to the axis of the sample, accurate to $2^{\circ}$. Since it would be very difficult to ensure that the ends of the samples were maintained perpendicular to the beam, they were placed near the point which is conjugate to the spectrometer slits. With the sample at this point it can be rotated several degrees about an axis perpendicular to the beam without displacing the image formed at the spectrometer slits. If the sample were not close to the point conjugate to the slits, such a rotation would cause a small displacement of the image and would, therefore, introduce considerable error in the measurements because of the variation in the signal as the image moves relative to the slits. Displacement of only a fraction of a millimeter could cause appreciable error.

The aperture stop in the system is placed at the flat mirror near the spectrometer as shown in Figure 1. By having the aperture between the sample and the spectrometer, the same portion of the prism in the spectrometer is "filled," regardless of any small displacement or deflection of the beam caused by the sample. It was found that this was necessary since the same small beam of radiation passing through different portions of the prism can result in quite different signals. This is due to a few factors, such as differences in the absorption by the prism, depending on the length of the light path through it and on the amount of light that is blocked off by the thermocouple located in the beam just ahead of the ellipsoid which focusses the radiation upon the thermocouple. Non-parallelism of the ends of the samples would tend to deflect the beam of radiation as it passed through; thus the portion of the beam going through the aperture stop would originate from different portions of the focussing mirror ahead of the furnace. In order to reduce errors caused by this deflection, the beam at this mirror was considerably over sized and attempts were made to maintain a uniform illumination over it so that a small deflection of the beam by the samples would not appreciably change the amount of radiation passing through the aperture. It was found that without taking this precaution considerable error was introduced unless the faces of the crystals were extremely close to being parallel.

The light shields at the ends of the furnace were stationary relative to the beam and did not limit the size of the main beam. Their purpose was to reduce extraneous light which might be scattered through the furnace. $CaF_2$ windows were used to reduce turbulence within the furnace which was especially bad at the higher temperatures with the ends of the furnace open. The windows were mounted to the stationary light shields rather than the movable furnace; thus the light beam passed through the same portion of the window regardless of the sample used or of the position of the furnace. Previous experience with the furnace had shown that one could expect a slight fogging of the relatively cold windows when the furnace was operated at high temperatures. By supporting the windows in this way negligible error resulted from any non-uniformity in their transmission. They were held against teflon O-rings which fit into grooves cut on the ends of the furnace; and although the seal was not leak-tight, it was sufficiently good that turbulence was virtually eliminated. It was found that if one of the windows was as far as 1 mm from the teflon seals, variations in the signal resulting from turbulence were large enough to cause considerable uncertainty in the measurements.

Two different prisms, LiF and NaCl, were used in the measurements. The dispersion of the LiF prism was so high for wavelengths less than 1μ and greater than 4μ that the signal-to-noise ration S/N was small. Therefore, a NaCl prism was used in order to get more accurate results at these wavelengths. Even with NaCl prisms the S/N was low for λ less than 1μ, so a photomultiplier was mounted on the spectrometer and used in this spectral region. The S/N was low because of the very narrow aperture which was used and because of the very small image which was formed on the spectrometer slits. The physical slit width used was approximately 1 mm which was wider than the image formed on them.

At a given wavelength the desired information could be obtained by measuring $D_O$, $D_S$, $D_L$, the recorder deflections observed with the light beam passing between the samples, through the short sample and through the long sample, respectively. Each of the recorder deflections was averaged over a period ranging from a few seconds to greater than one minute, depending on the signal-to-noise. All three readings were taken without changing the wavelength setting on the spectrometer. Wavelengths where the measurements were made are: 0.546, 0.60, 0.70, 0.80, 0.90, 1.00, 1.25, 1.50, 1.75, 2.0, 2.2, 2.25, 2.5, 3.0, 3.25, 3.5, 3.75, 4.0, 4.5, 4.75, 5.0, 5.25, 5.5, and 5.75 microns. None of these wavelengths occur in the regions of the strongest atmospheric absorption although there is slight absorption by $CO_2$ and $H_2O$ at some of these wavelengths.

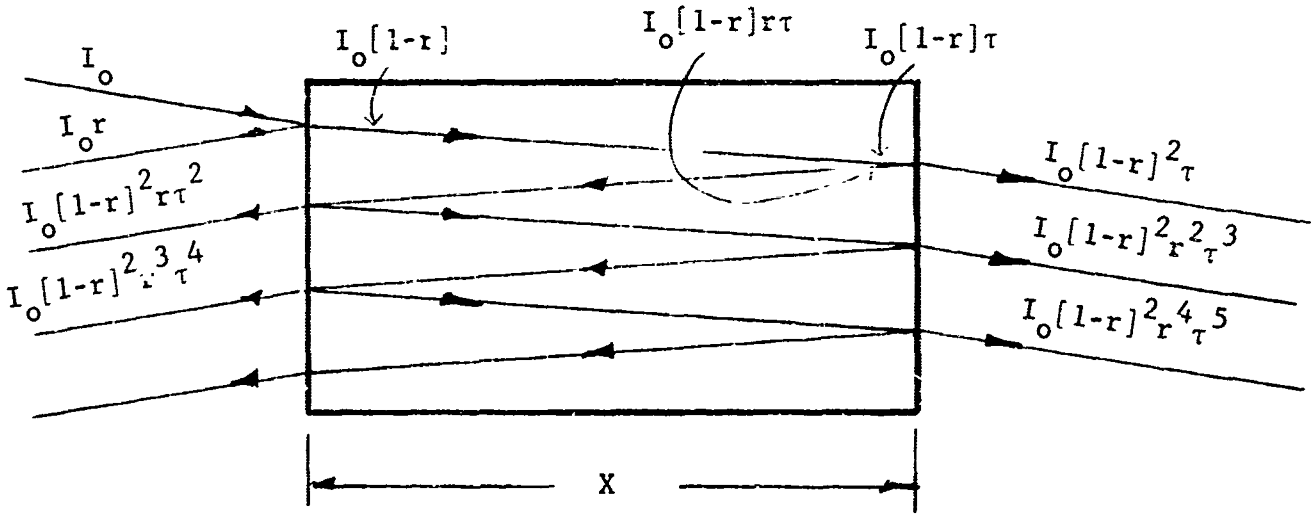

FIGURE 2-2 DIAGRAM OF THE REFLECTED AND TRANSMITTED COMPONENTS OF A BEAM. $I_o$ is the intensity of the incident beam and the intensities of the other components are as shown. The reflectivity at a surface is denoted by r and $\tau$ is the transmittance of a beam from a point just inside the surface at one end through the sample to another point just inside the surface at the other end.

The method of determining the absorption coefficient and index of refraction from the measurements can best be explained by the use of Figure 2-2 in which $I_o$ represents the intensity of an incident beam on a sample, and the intensities of the components of the beam after it has been transmitted and partially reflected at several surfaces are as illustrated. The reflectivity $r(\lambda)$ at a surface for wavelength $\lambda$ is related to the index of refraction $n(\lambda)$ by

$$r(\lambda) = \left[ \frac{n(\lambda) - 1}{n(\lambda) + 1} \right]^2 \qquad (2\text{-}1)$$

For the purpose of simplifying the expressions, we define

$$\tau(\lambda) = \exp\left[-k(\lambda)\, X\right], \tag{2-2}$$

where X is the length of the sample. The equations will be written without (λ) since they apply to a single wavelength. If one assumed that all of the rays from the right-hand end of the sample were accepted by the spectrometer and that the recorder deflections were proportional to the intensity of the beam, it can be seen that

$$\frac{D}{D_0} = (1 - r)^2 \tau \left[1 + r^2 \tau^2 + r^4 \tau^4 + \ldots\right] \tag{2-3a}$$

which can be written as

$$\frac{D}{D_0} = \frac{(1 - r)^2 \tau}{1 - r^2 \tau^2} \tag{2-3b}$$

Although (2-3b) has a simpler form than (2-3a), it is easier to determine the values of k and n by using an approximation method involving the series expression in (2-3a). From (2-3a) one can write

$$\frac{D_L}{D_0} = (1 - r)^2 \tau_L \left[1 + r^2 \tau_L^2 + \ldots\right] \quad \text{and} \tag{2-4}$$

$$\frac{D_S}{D_0} = (1 - r)^2 \tau_S \left[1 + r^2 \tau_S^2 \ \ldots\right] \tag{2-5}$$

where the subscripts L and S denote the long and short samples, respectively.

In order to determine k and n, we combine (2-1), (2-2, 2-4) and (2-5) and use a rather simple approximation method. First, all except the first term in the brackets of (2-3) and (2-4) are dropped. The ratio of these two equations then gives

$$\frac{D_L}{D_S} \simeq \frac{\tau_L}{\tau_S} = \frac{\exp\,(-k\,X_L)}{\exp\,(-k\,X_S)} = \exp\left[-k\,(X_L - X_S)\right] \qquad (2\text{-}6)$$

Since $D_L$ and $D_S$ are measured quantities, an approximate value of k can be calculated; then by use of (2-2) $\tau_L$ and $\tau_S$ can be approximated. By inserting the approximate value of either $\tau_S$ or $\tau_L$ into the appropriate equation (2-4) or (2-5) with only the first term in the bracket included, an approximate value of r can then be obtained. The approximate values of r, $\tau_L$, $\tau_S$ are then inserted in the second term in the brackets of equations (2-4) and (2-5) to determine a more accurate value of the quantity within the brackets. The ratio $\tau_L/\tau_S$ is then re-calculated by using this more accurate value, and from this ratio the more accurate value of k can then be determined. This new value of k is then used to determine the value of $\tau_S$ which is substituted into (2-5) to obtain the final value of r. Equation (2-1) is then used to determine n.

Carrying of more than two terms in equations (2-3) and (2-4) cannot be justified in view of the accuracy with which the signals can be measured. In fact, for many measurements the error introduced by ignoring the second term in the brackets would probably be less than the uncertainty of the measurements. The maximum value of r is approximately 0.08. Therefore, the maximum value of $r^2\,\tau^2$ is approximately 0.006. For cases where $\tau \ll 1$ the contribution of this term is even less, and the several steps in the approximation method can be ignored by merely assuming that all but the first term in the brackets are negligible.

It should be noted that several assumptions have been made in the discussion immediately above. First of all, it was assumed that the ends of the sample were flat and parallel. It was further assumed that there was no scattering or absorption due to foreign material on the surface. Either of these phenomena would tend to cause the calculated value of reflectivity to be too large if the scattering or absorption was the same on both samples. If the scattering or absorption were greater on the long sample than on the short one, one would tend to calculate too large a value for k and too small a value for r. Excessive scattering or absorption on the short sample would tend to give the opposite answer.

Before the samples were heated, measurements were taken at a couple of wavelengths at room temperature. The calculated values for the index of refraction based on these measurements were then compared to the published values which are known very accurately. If the agreement was not good the alignment of the optics was checked and the samples were checked for possible contamination on the ends or for cleavages within the crystals. A further check was made by observing the signal as a sample was moved slowly through the beam. Since the beam was considerably smaller than the diameter of the samples, they could be moved a distance of about 6 mm without changing the signal, provided the sample was uniform. This check was also made at the elevated temperatures before a set of measurements was made and at near room temperature after the samples had been allowed to cool. If they were found to be uniform, it was assumed that they had not fogged during the time the high temperature measurements were being made. Several sets of measurements were made at some of the temperatures, and the results shown in the next section represent what is believed to be the best values, with most weight being given to those obtained when the samples appeared to be uniform.

## 2.3 FLAME METHOD

Flames formed by burning $H_2$ in $O_2$ were used to heat samples of sapphire and ceramic aluminum oxide to temperatures which were higher than those attainable in the furnace. The primary objective of this part of the investigation was to obtain measurements on the samples just below and just above the melting point so that any change in the emissive properties of the sample which take place upon melting could be observed.

Figure 2-3 shows an optical diagram of the apparatus used to make absorption studies of sapphire samples. The sample and torches were mounted on a movable base which could be displaced in the direction indicated so that radiation from the Nernst glower could be directed either past the sample or through it. Light from a Nernst glower passed a chopper and was focussed on the sapphire samples; it was then re-focussed on a set of adjustable slits. The radiation passing through the slits was then focussed on the slits of the spectrometer. The purpose of the slits was to limit the size of the area of the sample which was being viewed to an area sufficiently small to be nearly uniform. This was necessary since the temperature of the sample was very nonuniform particularly at temperatures where a small portion of the sample was melted. Most of the data were obtained with the opening between the slits about 1/2 mm x 1/2 mm. The jaws of the slits were covered with white paper so that a rather sharp image of the hot sample could be seen on it, making it possible to see what portion of the sample was being observed.

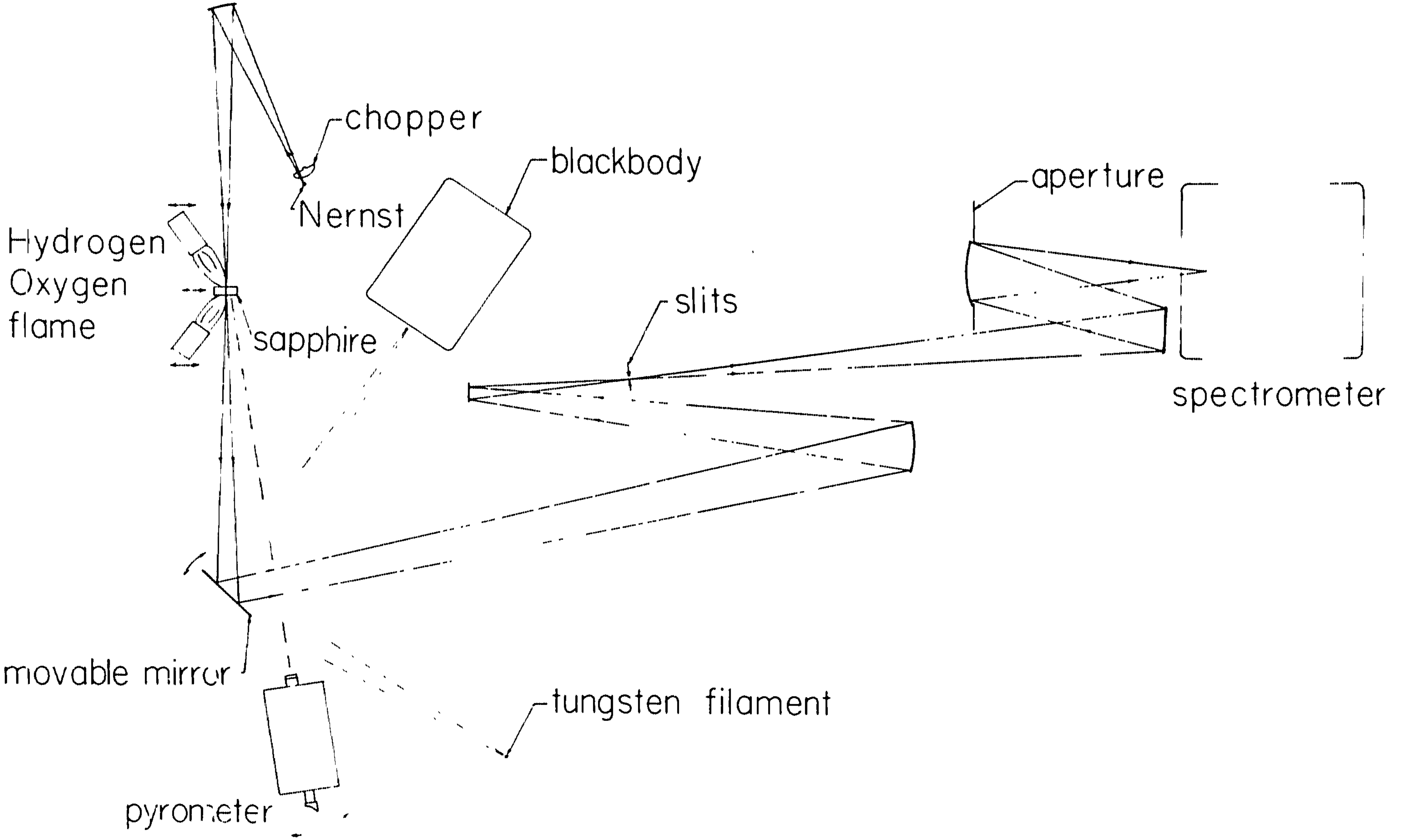

FIGURE 2-3 OPTICAL DIAGRAM OF APPARATUS USED TO STUDY SAMPLES HEATED WITH FLAMES. The transmittance of samples could be measured with arrangement shown. Emission measurements were made by blocking light from the Nernst and using a chopper inside the spectrometer. Radiation from either a blackbody at 925°C or a calibrated tungsten filament could be directed into the spectrometer for use as radiation standards.

The aperture stop was located on the mirror immediately preceding the spectrometer as shown in the figure and was considerably larger than that used in the furnace method. A photomultiplier and a thermocouple were used as detectors as in the furnace method. The spectrometer contained an NaCl prism, and the physical slit widths employed were about 300 microns for $\lambda \leq 3.5$ micron and 1200 microns for longer wavelengths.

In order to observe the emission by a sample, the Nernst glower was either turned off or the chopper blade was turned into the position so that radiation from the Nernst would not reach the spectrometer. The focussing mirror between the chopper and the sample was covered with black paper to prevent any radiation emitted from the sample toward the mirror from being reflected back into the beam entering the spectrometer.

Two radiation standards were used; one was a standard blackbody cavity maintained at approximately 925°C, and the other was a tungsten filament lamp which was operated at approximately 2000°C. The blackbody was useful for wavelengths greater than about 2μ, but because of its relatively low temperature the radiation at shorter wavelengths was very low. The tungsten filament was used as a standard for $\lambda < 2\mu$, and its radiation temperature was determined by using an optical pyrometer with a filter passing radiation of approximately 0.65μ. Values for the emissivity of the tungsten filament were taken from an article by J. C. de Vos[8] and used to determine the true temperature of the filament. Radiation from either the standard blackbody or the tungsten filament could easily be directed to the spectrometer by rotating the movable mirror to the proper position.

An optical pyrometer which is shown in Figure 2-3 was located so that the sample could be viewed by looking past the movable mirror. It could also be swung around into a position so that the tungsten filament could be observed. By viewing the sample one could determine its radiation temperature at the wavelength of the pyrometer filter; but since the emissivity of the sample was not known, it was not possible to determine the true temperature in this way. However, the pyrometer was very useful in viewing the sample and particularly in observing temperature gradients surrounding a small spot which was being maintained in a molten state. The optical system of the pyrometer could be focussed very sharply, and it provided sufficient magnification that spots of the sample as small as 0.1 mm in diameter could be observed clearly.

A photograph of the apparatus used in the flame method is shown in Figure 2-4, where many of the components are labelled. Figure 2-5 shows a close-up view of the torches and sample mounted on a movable base.

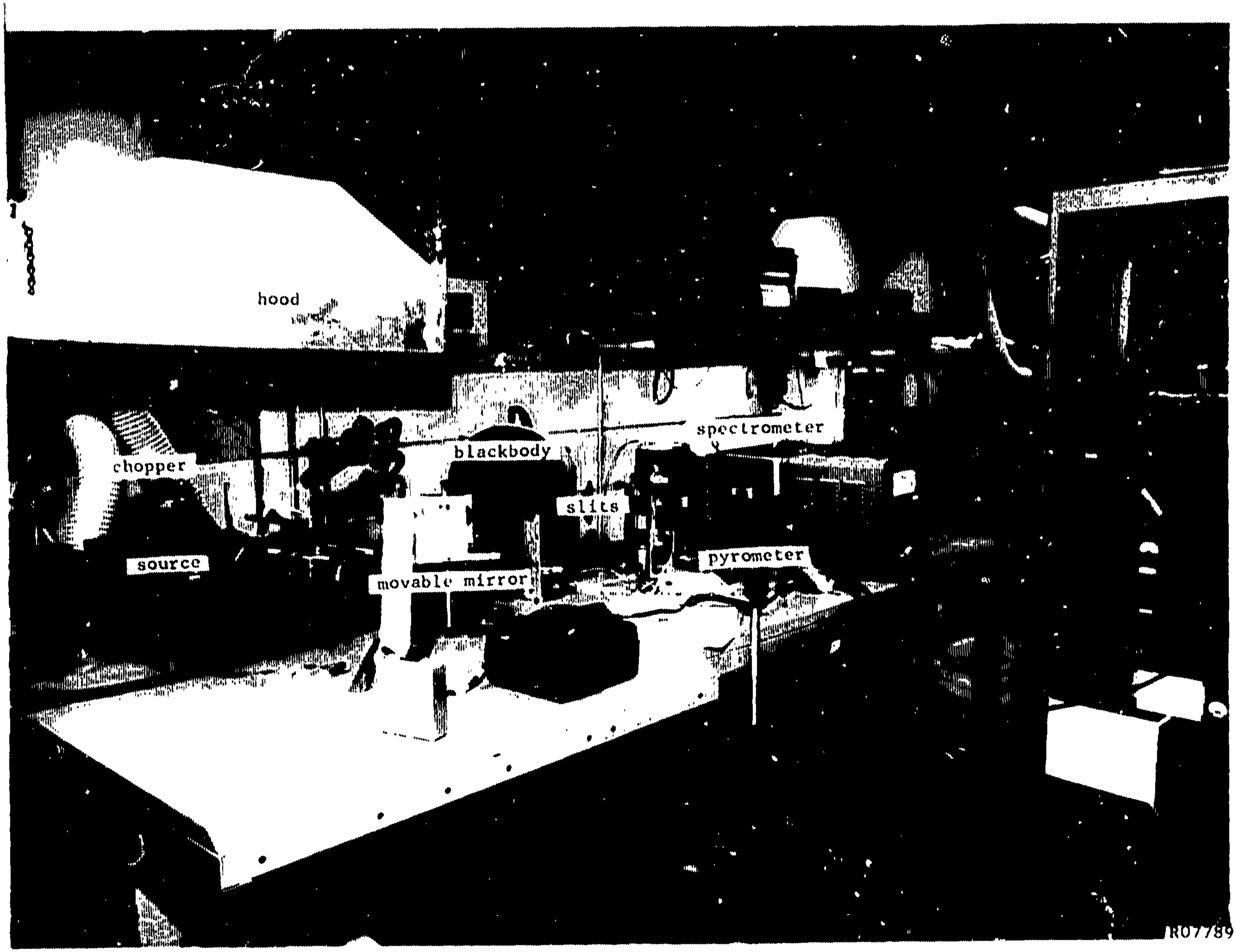

FIGURE 2-4 PHOTOGRAPH OF APPARATUS USED TO STUDY SAMPLES HEATED WITH FLAMES. Some of the components are labelled and several others can be identified by comparison with the optical diagram in Fig. 2-3. The apparatus in the background was not used as a part of this investigation. The recorder is not shown.

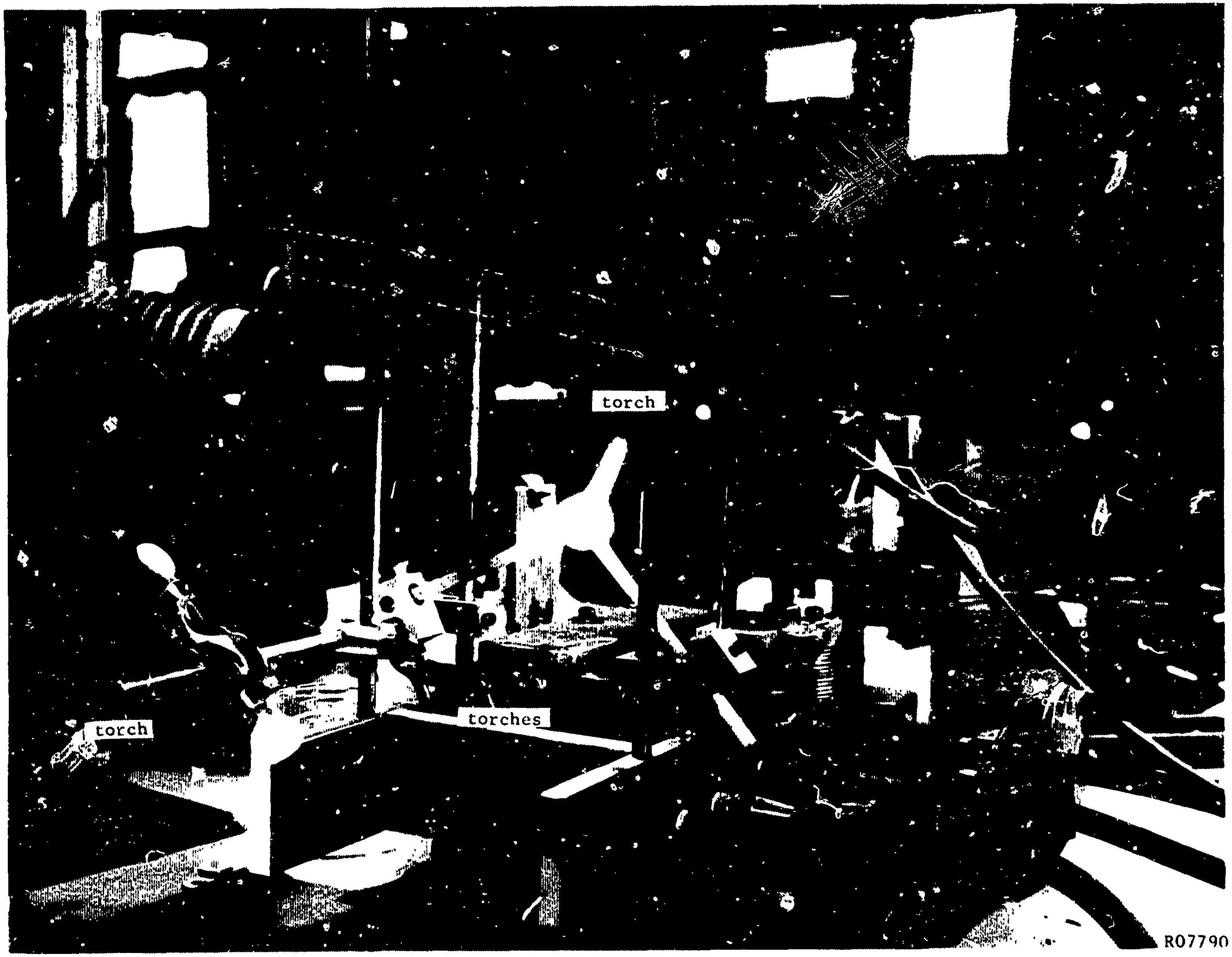

FIGURE 2-5 CLOSE-UP VIEW OF TORCH AND SAMPLE MOUNTED ON MOVABLE BASE. The blackbody can be seen on the left. Four torches (not burning) were water cooled and provided heat from below. Another torch shown in left foreground was used to attain highest temperatures. The sample and torches were mounted on the movable base in order that different portions of the sample could be viewed, and it could

Three different methods were used to obtain approximate values of the temperature of the samples being studied; the method used depended on the material and the temperature. The first could be used on sapphire samples whose ends were polished flat and parallel so that the transmittance could be determined by comparing the signal observed from the Nernst glower with the sapphire sample in the beam to that observed with it displaced out of the beam. The value of the reflectivity of the sample was estimated from the results of the measurements made by the furnace method and was inserted in Equation (2-3a) where all but the first term in the bracket was neglected to determine the value of $\tau$. It will be seen in Section 3.4 that the index of refraction of sapphire does not depend strongly on temperature; therefore, the reflectivity can be approximated from measurements made at somewhat different temperatures. If one considers only the rays emitted from the sample in the direction of the spectrometer and ignores all those rays which are internally reflected at the surfaces, it can be shown that the emissivity $\epsilon$ is given by

$$\epsilon = (1 - r)(1 - \tau) \tag{2-7}$$

The emission by the sample and that by the standard blackbody at the same wavelength were then measured. We define $D_e$ as the recorder deflection observed from the emission of the sample and $D_b$ as the deflection from the blackbody. $R_b(T)$ is the radiation from a blackbody at T, the temperature of the sample, and $R_b(T_b)$ is the radiation from the standard blackbody at its temperature $T_b$, which in this experiment is approximately 925°C. $R_b(T)$ can then be found by the following equation:

$$R_b(T) = \frac{D_e}{D_b} \frac{R_b(T_b)}{\epsilon} \tag{2-8}$$

Tables of the blackbody function then can be used to determine the temperature of the sample. This method of determining the temperature is satisfactory if there is appreciable absorption by the sample, in which case $\tau$ is considerably less than one. The temperature was usually measured by this method at two or three wavelengths with the standard blackbody source being used for $\lambda$ greater than $2\mu$ and the tungsten filament for shorter wavelengths. For samples in which there was appreciable absorption the temperatures determined at the different wavelengths were usually in agreement to approximately ± 30°C. It was necessary to carefully select the wavelength at which the measurements were made in order to avoid error due to emission and absorption by the water formed in the flame.

The second method of determining the temperature was very much like the first, except that no transmission measurement was made. It is useful for sapphire samples in which the ends are not flat or for ceramic $Al_2O_3$ in which the many small crystals act as scatterers. At wavelengths beyond approximately 5μ, $\tau$ is approximately equal to zero for any sample more than a few mm thick; therefore, $\tau$ in Equation (2-7) can be assumed to be equal to zero. The biggest source of error in this method arises from the uncertainty in the value of r which should be used. For sapphire, r can be approximated by using the values of n which have been measured at lower temperatures. However, in the case of the ceramic material, the small crystals act as scatterers and an effective reflectivity would be difficult to calculate when the scattering cross-section is not much smaller than the absorption cross-section in the material. It was found that if one used $r = 0.1$ at 7μ, the temperature determined for a ceramic sample just before it started melting was in reasonable agreement with published values of the melting point.

The third method of measuring the temperature involved using the fact that the melting points of sapphire and the ceramic material are known to be approximately 2040°C and 2000°C, respectively. By carefully adjusting the flames it was possible to maintain a small spot on the surface of a sapphire crystal in the molten form, and by viewing it through the pyrometer, the outline of the melted portion was seen to be rather sharp. As will be discussed in Section 3.2 a melted portion was found to be much brighter than the solid portion only a fraction of a millimeter away. One can use published values of the heat conductivity of sapphire to show that the temperature of the nearby unmelted portion could not be more than a few degrees lower than the melting point. The radiation temperature of the portion near the melted spot could be measured with the optical pyrometer, and it was assumed that any other portion of the sample which was a short distance away and had the same radiation temperature was actually at the same temperature. By using this technique it was possible to study a portion of a sample of sapphire which was 1 mm thick and was believed to be at a temperature of approximately 2020°C. This temperature could almost certainly not be more than 20° too low or more than 40 or 50° too high.

It should be noted that it is not possible to determine the temperature of a sapphire sample with an optical pyrometer by observing a cavity which has been drilled into the sample. The absorption coefficient of the sapphire in the visible region is so small that the cavity does not approximate a blackbody. A small cavity with a diameter of approximately 1 mm and a depth of about 4 mm was lined with a graphite in an attempt to obtain a nearly black cavity. This, too, was unsatisfactory since the temperature of the cavity was considerably lower than that of the sample. This was true because most of the heat was transferred to the cavity by radiation from the sapphire and, for wavelengths near the peak of the blackbody curve of the sample temperature, the emissivity of the sapphire is rather low. Therefore, the cavity could not be heated to the temperature of the sample. In addition, the graphite was essentially black and could radiate in every direction, out through the sapphire sample as well as out through the end of the cavity; thus, its equilibrium temperature was well below that of the sample. The temperature measured by observing this type of cavity was compared with the temperature determined by the second method described above and was found to be a few hundred degrees low.

More will be said about some of the experimental methods in the discussion of the results in Section 3.

# SECTION 3

# RESULTS AND DISCUSSION

## 3.1 ABSORPTION COEFFICIENT FOR SAPPHIRE

The results of the measurements of the absorption coefficient $k(\lambda)$ for solid sapphire are summarized in Figure 3-1. Data for all of the curves except the upper one, which corresponds to a temperature of 2020°C, were obtained by the furnace method. The curves are drawn over the wavelength range for which measurements were made. In this investigation we were not interested in the wavelength region beyond about $6\mu$ since most of the emission from hot flames occur at shorter wavelengths. Although the major interest was in temperatures above 1500°C, the measurements were made at lower temperatures in order to develop the techniques and to obtain results that could be compared with those of previous workers. It was also desirable to see if there were any anomalous effects or particularly interesting changes in the absorption coefficient with temperature. As mentioned in Section 2-2, the measurements were made at several different wavelengths, and the curves shown in the figure were obtained by drawing smooth curves through these points. A few spectra were scanned at a couple of different temperatures and no structure other than that which is shown in the curves was observed except for that which could be attributed to the absorption by $CO_2$ and $H_2O$ in the atmospheric path.

In order to present the curves for all the temperatures in a single figure without clutter, the data points were omitted. The curves shown actually represent several different sets of measurements which were made on different days. In attempting to determine the best fit to the data, extra weight was given to those results obtained when the samples appeared to be particularly uniform.

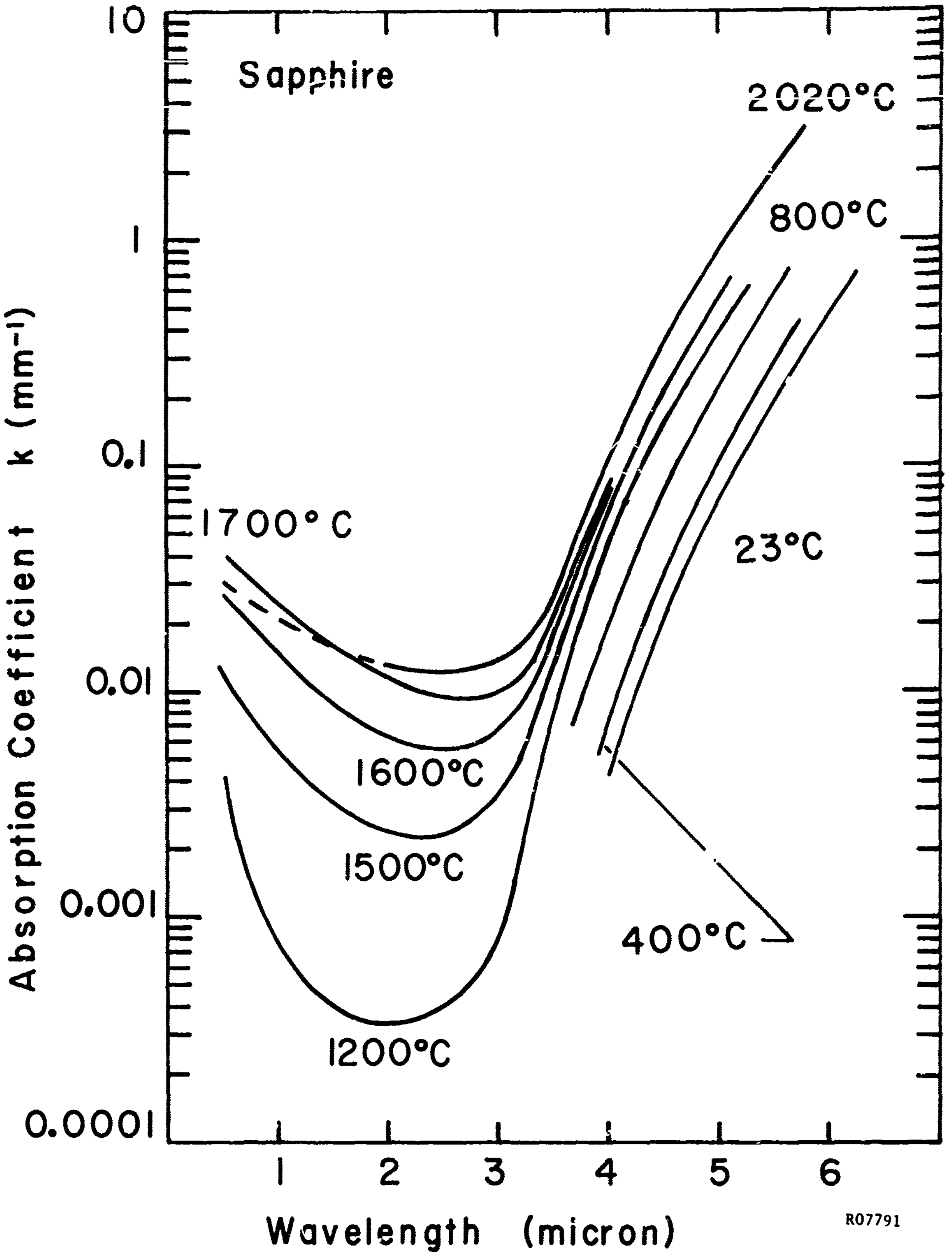

FIGURE 3-1 ABSORPTION COEFFICIENT OF SAPHIRE AS A FUNCTION OF WAVELENGTH FOR VARIOUS TEMPERATURES.
Data for the curve corresponding to 2020°C were obtained by heating the samples with flames while a furnace was used for the remainder of the data.

For values of k less than approximately 0.001, the results may be in error by as much as ± 30%. This rather large uncertainty arises from the fact that for even the longest sample used, 25.4 mm, the attenuation caused by absorption is only a couple of percent which is considerably smaller than the approximately 15% attenuation by reflection. When the absorption is small, a slight error arising from scattering or from misalignment of the crystals could cause appreciable error in the calculated value of the absorption coefficient. The values shown for k equal to approximately 0.01 are probably accurate to better than 10 or 15%.

Three or four features of the curves are very apparent. With the exception of the portion of the 2020°C curve below about 2μ, it is seen that the absorption coefficient increases with temperature. For example, at wavelengths below approximately 2.5μ, the absorption coefficient increases by approximately a factor of 20 in going from 1200° to 1700°C; although there is still an increase with temperature at longer wavelengths, it is less striking than for the shorter wavelengths. The portion of the 2020°C curve below 2μ is shown as a broken line to indicate that the uncertainty is considerably larger than for most of the other curves. Part of this large uncertainty arises from the fact that a small error in the assumed temperature of the sample heated by the flame method would introduce considerable error in the calculated value of the absorption coefficient because of the strong dependence of the emission by a blackbody on temperature at these wavelengths. Although this is the only portion of the data which shows a decrease in absorption coefficient with temperature and the uncertainty is rather large (± 30%), it is believed that the decrease as one goes from 1700°C to 2020°C is real.

A minimum in the curves is seen to appear between approximately 1.8 and 2.7μ with the minimum shifting towards longer wavelengths at higher temperatures. The exact position of the minimum would be difficult to determine because of the interference of the absorption by water vapor near 2.7μ. The curves are also seen to crowd together in the region between 3.5 and 4.0μ and show a very strong dependence on wavelength.

In order to compare the flame method with the furance method, both were used to determine values of k at temperatures between 1200°C and 1700°C. The results of the flame method showed considerably more scatter than those obtained by the furnace method, but the agreement was in general pretty good. This agreement tends to give one more confidence in the results obtained by the flame method, and leads one to believe that the curve corresponding to 2020°C is reliable.

The values of k which have been determined in this investigation show the same general dependence on wavelength and temperature as those of previous workers. However, there is considerable discrepancy between the published results, so that there is some doubt as to which ones should be used to compare with our values at a specific wavelength for a certain temperature. Since Monroe[7] has published a curve of the apparent transmission of a 1.97 mm sample, one can allow for the reflection losses by using our results given in Section 3.4 to calculate k. His results are of interest since he has a curve for 1500°C which is higher than any of the temperatures used by other workers. As an example at 5μ, and 1500°C, we calculate from his results a value of $k = 0.26$, which is to be compared with 0.54 obtained by us. Mergerian[3] shows curves of the absorption coefficient versus wavelength for 100°C, 350°C, 750°C and 1000°C. They have the same general shape as those in Figure 3-1 with a minimum in the 2-3μ region. The agreement with our results is not good for $\lambda < 3\mu$.

## 3.2 EMISSION BY MOLTEN SAPPHIRE

Most of the data obtained on the emission by molten sapphire is only semi-quantitative since it was difficult to reproduce conditions exactly and to characterize the spot being used. The melted portion was very easily distinguished since it appeared much brighter when viewed through the optical pyrometer, and the edges of the melted portion were very distinct. By making fine adjustments on the movable flat mirror shown in Figure 2-3, one could measure the radiation from any desired portion of the sample. The solid spot which could be observed was approximately 1/2 mm by 1/2 mm.

As a typical example, a melted spot 3 or 4 mm in diameter on a sapphire crystal which was 1 mm thick might have a radiation temperature of 1850°C at 0.65 microns, the wavelength passed by the filter in the pyrometer. By comparison the radiation temperature at a point considerably less than 1 mm from the edge of the melted portion would be 1450°C. By comparing the radiation from a blackbody at these two temperatures, one finds that the brightness of the melted spot is approximately 10 or 12 times that of the adjacent spot which is still in a solid form. Because of the fact that the two spots where the radiation temperature was measured were so close together, and since the samples were heated by three or more flames positioned so as to minimize temperature gradients in the crystal, one is led to believe that the actual temperature difference between the two points could not be more than a few degrees centigrade. Therefore, the large increase in the emission is believed to be due to the difference between the solid and the molten state. As nearly as one could tell by viewing the samples through the pyrometer, the increase in brightness appeared at the same time that one could see slight movement of the sample which appeared much like a drop of liquid with a high surface tension on a solid surface.

Although the size of the melted spot could be maintained reasonably uniform, the radiation from it varied by as much as ± 10% with a typical period of 4 or 5 seconds. Because of this variation in time, it was not practical to attempt to scan an entire spectrum with the hope of seeing any changes with wavelength. In order to see if the sudden increase in brightness also appeared in the infrared portion of the spectrum, several measurements were made at 2.2μ by using the spectrometer. This wavelength was chosen since it occurred near the minimum in the absorption coefficient curve, and since it was relatively free of emission by the flame. The results obtained at this wavelength were very similar to those obtained at 0.65μ with the optical pyrometer. It was typically found that the brightness of a melted spot was 15-20 times as large as that of an unmelted spot which was not more than a mm away.

It is difficult to say what the sudden change in brightness means in terms of the absorption coefficient k. The radiation emitted can be measured with reasonable accuracy, but the greatest uncertainty occurs in trying to determine the thickness of the melted portion which is being viewed. When the 1 mm thick sample was being studied, it was probable that the depth of the melted spots was not more than 1/4 or 1/3 mm. If this were the case, one is led to believe that the absorption coefficient k actually increases by a factor of as much as 30 or 40, and possibly even more. A factor of 20 is almost certainly a minimum; therefore, the absorption coefficient at 0.65μ and at 2.2μ is estimated to be of the order of 1 $mm^{-1}$ for just above the melting point. Although spectra of the entire wavelength region were not obtained for the molten sapphire, the very marked increase in brightness which appears upon melting was seen to be prevalent at wavelengths below about 4μ. One would not expect such a marked increase in the brightness of samples beyond 4μ since the emissivity of even the 1 mm sample could become sufficiently large that a further increase in k would not cause a large change in the brightness.

As a separate part of this project, Don Carlson[9] has measured the emission from aluminum oxide particles in rocket flames. His measurements covered ranges of temperature over which the aluminum oxide particles pass through the melting point, and his results are in general agreement with ours. The continuum radiation which he observed was attributed to the emission by the aluminum oxide particles and was found to be very low when the particles in the exhaust were in the solid phase, but at temperatures for which the particles were known to be in a liquid phase a sizeable continuum emission appeared.

Because of the large increase in absorption coefficient which has been observed as the temperature is increased from around 1200°C to the melting point and above, it can be concluded that previous calculations on the emission one would expect from aluminum oxide particles in flames should be redone with more realistic values of the absorption coefficient than those which were available before.[1,2]

## 3.3 EMISSION BY POLYCRYSTALLINE $Al_2O_3$

Emission measurements were made using the flame method on a few pieces of ceramic $Al_2O_3$ whose purity is supposedly about 99.7%. Samples were polycrystalline with the sizes of the crystals varying from less than 1μ to several microns. Little else is known about the size distribution or about the sizes of the holes between the crystals. Since these samples were nearly pure $Al_2O_3$, it seemed of interest to see if emission properties were similar to those of the single crystalline $Al_2O_3$.

In a previous experiment which was carried out in our laboratory it was found that a piece of $Al_2O_3$ 1 mm thick would transmit approximately as much through it as was absorbed. Since the material is a very good scatterer, a large portion of light incident upon a sample is scattered back, and the actual path of a ray traversing from one surface through the material and out the other surface would be several times the thickness of the material. On the basis of the earlier experiment one is led to believe that the absorptivity of any impurities which might be present is not too large, and that the emissivity of the sample at room temperature would be small.

A theoretical calculation of the emissivity of a sample where the scattering cross-section is large compared to the absorption cross-section is very difficult, but the problem has been investigated by Dr. Ernest Bauer[1] of Philco Research Laboratories who found that it was necessary to make several assumptions in order to obtain quantitative results. However, it could be seen from the calculations that a sample will have an emissivity considerably less than 1/2 when it absorbs the same amount of radiation as is transmitted through it and when its scattering mean free path is small compared to its absorption mean free path and to its thickness. Therefore, a sample 1 mm thick would be expected to have an emissivity much less than 0.5 at room temperature. It was also found that when a small piece of ceramic $Al_2O_3$ was heated in a flame that it appeared rather bright, indicating that its emissivity was not exceptionally small. This increase in emissivity with temperature is, of course, consistent with the increase in absorption which is shown in Figure 3-1.

Because of this apparent increase in emissivity with temperature, it was decided that some semi-quantitative measurements would be attempted. The most difficult part of the experiment was in determining the temperature of the sample. Approximate temperatures could be determined by comparing the emission of a "hot" sample at about 8μ with that from the standard blackbody at the same wavelengths. Since the absorption coefficient of pure aluminum oxide crystals is known to be high at this wavelength, it could be assumed that the emissivity of the ceramic material would also not be greatly different from unity. This assumption was borne out by a measurement which showed that the emission from a small cavity in the material at this wavelength was only about 10 or 20% greater than the emission from a point very near the cavity which could be assumed to be at approximately the same temperature. If the emissivity of the material were very low at this wavelength, one would expect the emission from the cavity to be considerably greater than that from the nearby point. An approximate temperature was determined by assuming unit emissivity of the cavity at 8μ. Temperatures determined by this method were usually within 50 or 100°C of the temperature at which the material is believed to melt. Although this does not represent a good accuracy in the measurement of the temperature, it was sufficient to enable us to observe rather large changes in the emissive properties in the material.

The emissivity was found to increase with temperature throughout the region from the visible to 4μ as one went from approximately 1000°C up to just below the melting point. The emissivity was also found to be considerably less at about 2.2μ than in the visible or at longer wavelengths. These two results are consistent with those shown in Figure 3-1.

The emissivity of a piece of ceramic approximately 1 mm thick was seen to be a few times as great as that of a single crystal piece of sapphire at the same temperature. This difference could well be the result of impurities within the ceramic material. The emissivity of the ceramic material was also seen to increase sharply as one passed through the melting point. By assuming that the temperature of a molten spot was 2000°C, it was found that the emissivity of such a spot might vary from approximately 0.2 to 0.4. Since the depth of the molten material is not known and since it would be difficult to account for the emission by the solid material, it is impossible to directly relate this emissivity measurement to an absorption coefficient for a single crystalline material. It was found that the emissivity of a piece of the material was not increased substantially by increasing its thickness to more than 1 or 2 mm.

Very little in the way of quantitative information was obtained from the measurements of the emission of the ceramic material except to confirm the general behavior of the emissivity of $Al_2O_3$ as the temperature is increased up to and through the melting point. It was also found that although the material is polycrystalline and is a very diffuse scatterer, the emissivity which is related to the absorption coefficient k has a minimum at approximately 2.2μ and increases greatly as one goes towards longer wavelengths.

## 3.4 INDEX OF REFRACTION OF SAPPHIRE

Although the method of determining the index of refraction n by measuring the reflectivity is not an accurate one, it was good enough to permit one to allow for reflection losses in determining the absorption coefficient. The primary purpose of this investigation is to determine reliable values of the absorption coefficient k(λ), and to see if there are any very significant changes in n as the temperature is increased. From the scatter in our data one would estimate that n could not be measured with an accuracy better than 0.02 or 0.03, which is a few orders of magnitude worse than the accuracy of measurements which have been made near room temperature by other techniques.

Our results indicate n increases by about 0.04 or 0.05 in the region from 0.56 to 4 microns in going from room temperature to 1700°C. It is noted that the measured increase is only about twice as large as the uncertainty in the measurements. It is also more probable that the measured increase is too large than too small since any attenuation at the surfaces of the crystals by "fog" would appear as a reflection loss. In view of this fact, the change in n in going from 23°C to 1700°C is estimated to be $0.05^{+0.01}_{-0.03}$.

Malitson[10] has measured n for sapphire at 17°, 24° and 31°C and has found that (dn/dT), the change of the refractive index with temperature, was positive and decreased from about $2 \times 10^{-5}/^{\circ}C$ at short wavelengths to about $10^{-5}/^{\circ}C$ near 4μ. If one used a mean value of $1.5 \times 10^{-5}/^{\circ}C$ and assumed it was valid up to 1700°C, an increase of 0.026 in n would be calculated. This value is seen to be consistent with our results, and one is led to conclude that (dn/dT) probably does not change greatly in the region from the visible to $4\mu$ as the temperature is increased to 1700°C.

No significant variation in the change in n with $\lambda$ could be observed in our data. The measurements of n for $\lambda > 4\mu$ are not very reliable since even the shortest sample absorbed more than 50% of the radiation so that the reflection loss could not be measured accurately.

# SECTION 4

## REFERENCES

1. F. Bauer and D. J. Carlson, J. Quant. Spec. and Rad. Transfer, 4, No. 3, 363, (1964).
2. G. N. Plass, Appl. Opt. 3, No. 7, 867, (1964).
3. D. Mergerian, Proceedings of Infrared Information Symposium, 4, No. 4, 146, (1949).
4. U. P. Oppenheim and U. Even, J. Opt. Soc. Am., 52, 1078, (1962).
5. E. D. McAllister, Proceedings of Infrared Information Symposium, 4, No. 4, 139, (1949).
6. D. W. Lee and W. D. Kingery, J. Am. Ceram. Soc., 43, 594, (1960).
7. James E. Monroe, Jr., Final Report, Contract NOnr 1503(02), NR 032-022, U. S. Office of Naval Research, Metallurgy Branch, Alfred Univ., Alfred, New York (1957).
8. J. C. de Vos, Physica, 20, 690 (1954).
9. D. J. Carlson and R. A. DuPuis, Final Technical Report, Contract NOnr 3606(00), ARPA, Aeronutronic Publication No. U-2627, 31 May 1964.
10. Irving H. Malitson, J. Opt. Soc. Am. 52, 1377 (1962).