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NOVEL MATERIALS FOR POWER SYSTEMS. PART III. SELECTIVE EMITTERS FOR ENERGY CONVERSION

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13. ABSTRACT

The work performed under this program can be subdivided into three areas: PART I - Schizophrenic Catalysts; PART II - Protonic Semi-Conductors; and PART III - Selective Emitters for Energy Conversion.

PART III - Selective Emitters for Energy Conversion

The first year goals were to determine those materials which would be most promising for use as selective emitters, to fabricate initial samples for testing, to build an optical system capable of measuring the spectral efficiency rapidly, and accurately, and to make initial measurements on the spectral efficiency of promising samples. All of these goals have been met.

It has been determined that the rare earth oxides and mixtures of rare earth oxides are quite promising as selective emitters for energy conversion. Initial samples of erbium oxide and mixtures of erbium oxide and ytterbium oxide have been fabricated. An optical system for measuring spectral efficiency has been built and preliminary tests run for measuring the spectral efficiency of these materials. The spectral efficiency measurement apparatus incorporates an automatic data acquisition system which allows the rapid processing of large numbers of samples.

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PART III

Selective Emitters for Energy Conversion

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Selective Emitters for Energy Conversion

by R. J. Schwartz

SUMMARY

A. Technical Problem

The objective of this investigation is to obtain a material which will radiate at high intensities (1-20 w/cm^2) in a relatively narrow predetermined wavelength range when it is thermally excited at high temperatures (1500°C - 2000°C). The motivation for this particular investigation is that the conversion efficiency of photovoltaic energy convertors can be made extremely high, provided that the radiation which is converted by the photovoltaic cell has a high spectral efficiency.

B. General Methodology

One means of obtaining the high spectral efficiency which is desired is by means of energy transfer between rare earth ions such as is utilized in present day laser material technology. It has been determined that the rare earth oxides and mixtures of the rare earth oxides are particularily promising in this regard.

One of the original goals of this investigation was to establish a measurement capability such that the large number of potentially promising samples could be measured rapidly and accurately.

C. Technical Results

The first year goals were to determine those materials which would be most promising for use as selective emitters, to fabricate initial samples for testing, to build an optical system capable of measuring the spectral efficiency rapidly and accurately, and to make initial measurements on the spectral efficiency of promising samples. All of these goals have been met.

It has been determined that the rare earth oxides and mixtures of rare earth oxides are quite promising as selective emitters for energy conversion. Initial samples of erbium oxide and mixtures of erbium oxide and ytterbium oxide have been fabricated. An optical system for measuring spectral efficiency has been built and preliminary tests run for measuring the spectral efficiency of these materials. The spectral efficiency measurement apparatus incorporates a automatic data aquisition system which allows the rapid processing of large number of samples.

D. Implications for Further Research

This program was initially proposed as a three year program. Funding support through ARPA has been terminated at the end of the first year. However, the program will be continued under NSF-MRL funding for a second year. It is expected that many of the major goals of this program can be met during the second year.

Selective Emitters for Energy Conversion

I. Introduction

The objective of this investigation is to obtain a material which will radiate at high intensities (1-20 w/cm^2) in a relatively narrow, predetermined, wavelength range when it is thermally excited at high temperatures (1500°C-2000°C).

The motivation for this particular investigation is that the conversion efficiency of a photovoltaic energy converter can be extremely high, provided the radiation which is to be converted by the photovoltaic cell satisfies certain conditions. The conditions which must be met by the radiation spectrum will be discussed in detail below. Briefly stated however, they are that the radiation be confined to wavelengths with energies just above the absorption edge of the semiconductor used to fabricate the photovoltaic cell and that the radiation intensity be high (1-20 w/cm^2).

II. Background Material

A. Factors Which Determine the Specifications to be Met by the Selective Emitter.

In order to determine the criteria to be met by the selective emitter, it is helpful to consider in some detail, the manner in which such an emitter will be utilized in an energy conversion system.

An energy conversion system of this type is known as a thermophotovoltaic (TPV) system. A schematic diagram of such a system is shown in Figure 1. The thermal source shown in this figure can be fossil, nuclear or solar in origin. The only requirement on the source is that it be capable of sufficiently high temperature operation that the radiation intensity from the selective emitter exceeds approximately 1 watt/cm^2.

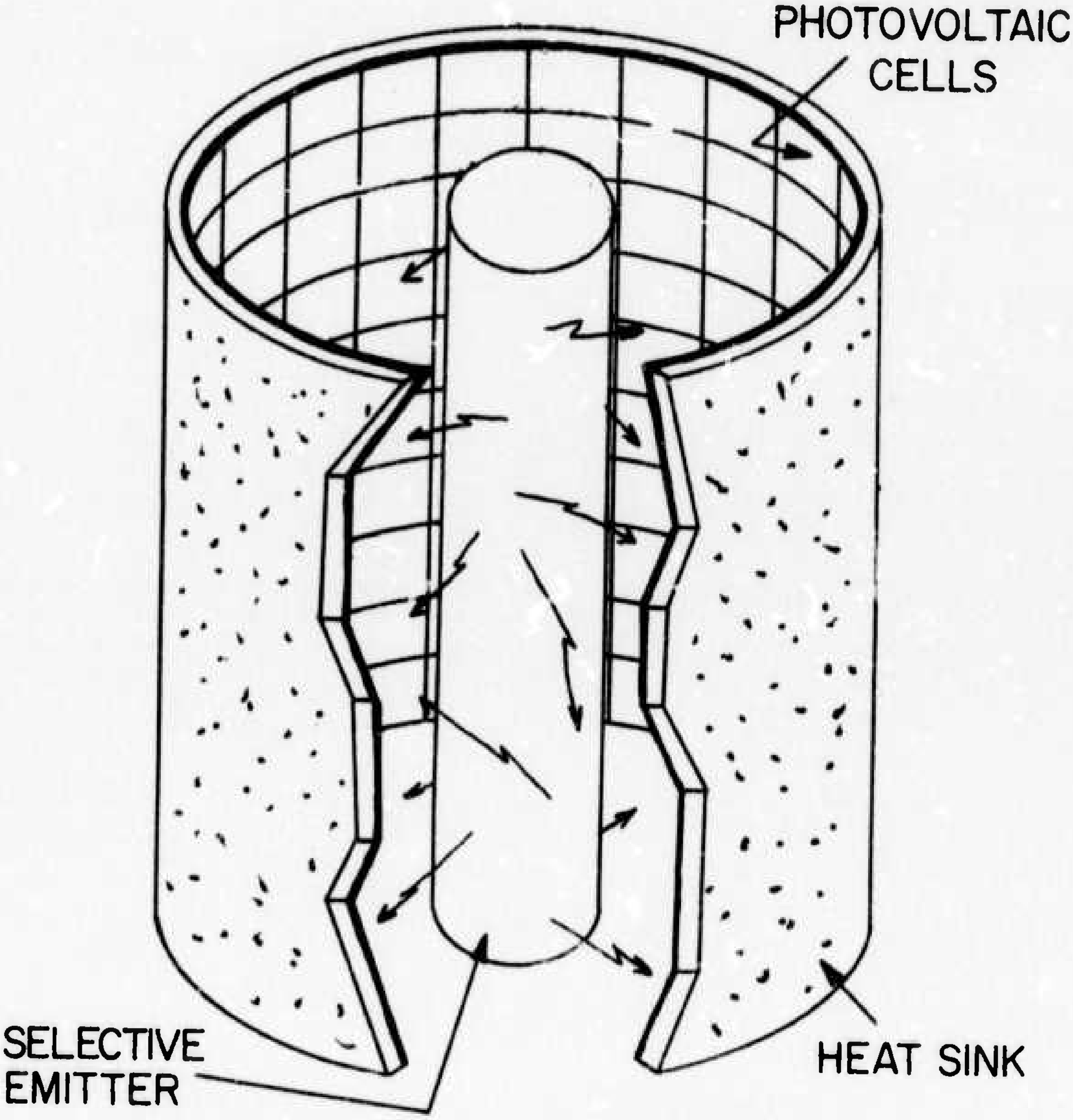

FIGURE 1. THERMOPHOTOVOLTAIC ENERGY CONVERTER.

In principle, the system can include an optical filter as well as a selective emitter to further enhance the spectral efficiency of the radiation spectrum. If such a filter is included in the system, the energy which is removed from the spectrum must be returned to the source. A thin film multilayer interference filter would be an example of such a filter.

Since it is the photovoltaic cell and the manner in which it converts the radiation into useful electrical energy which determines the requirements on the selective emitter,we shall discuss the factors which effect the conversion efficiency of the photovoltaic cell next.

Photovoltaic cells have been used as solar energy converters in numerous applications. While the requirements on the photovoltaic cell are similar for TPV and solar applications, there are significant differences, produced by the fact that one has control over the radiant source spectrum in the TPV case. Wolf[1] has enumerated the factors which effect the conversion efficiency of a photovoltaic cell. These factors apply equally well to TPV systems. They are:

1. The fraction of the incident radiation energy absorbed in the semiconductor bulk.
2. The fraction of the absorbed photon energy utilized for creation of hole-electron pairs.
3. The fraction of the optically generated hole-electron pairs that are collected at the p-n junction (collection efficiency).
4. The ratio of open circuit voltage to energy gap potential, (voltage factor).

5. The ratio of the maximum power point voltage times the maximum power point current to the open circuit voltage times the short circuit current, (curve factor).

The influence of each of the above factors on the specifications placed on the selective emitter will now be discussed.

Item 1. The fraction of the incident radiation energy which is absorbed in the semiconductor bulk depends on the absorption characteristics of the semiconductor and the spectral distribution of the radiator. As would be expected those photons with energy less than the semiconductor electronic energy gap are only weakly absorbed and have only a small probability of creating a hole-electron pair. The absorption coefficient is observed to increase by 2 to 4 orders of magnitude at the band edge. Thus, it is apparent that the emissivity of the selective radiator should be a minimum for energies less than the energy gap of the semiconductor chosen for the photovoltaic cell.

Item 2, places a similar restriction on the emissivity of the radiator for energies well above the electronic energy gap of the photovoltaic cell semiconductor. In this case the cut-off point is not sharp, however. When a hole-electron pair is created by the absorption of a photon, the photon energy in excess of the band gap energy is lost to the lattice as heat and is not recoverable by photovoltaic means.

Item 3. The collection efficiency is primarily determined by the dimensions of the photovoltaic cell, the lifetime of the hole-electron pairs in that cell, and the spectral distribution of the hole-electron pairs.

If the energy of the emission spectrum is primarily concentrated near an energy which corresponds to the direct band gap of the semiconductor, the radiation will be absorbed very near the incident surface. If the energy is primarily concentrated near the indirect gap energy, then the radiation will penetrate for a considerable distance before creating a hole-electron pair. Thus, in designing the photovoltaic cell one must take care that the carriers are generated within approximately a diffusion length of the p-n junction. Obviously, if the energy is distributed throughout both these regions one has to strike a compromise and the collection efficiency is reduced. Also, in most semiconductors there is a serious problem with maintaining a very low surface recombination velocity. This means that if the energy in the incident radiation is concentrated near the direct gap energy and the carriers are generated very close to the surface, the carriers are especially susceptible to surface recombination and the collection efficiency is thereby reduced.

Items 4 and 5. The voltage factor and the curve factor are primarily determined by the construction details of the photovoltaic cell and the choice of semiconductor material which is used in fabricating the cell. However, they are also influenced by the intensity of the incident radiation. Both the voltage factor and the curve factor will tend to be larger at higher incident intensities, if the cell is properly designed.

B. Choice of Radiative Materials

The requirements, which have been outlined above, for efficient thermophotovoltaic energy conversion can now be summarized in terms of the requirements which are placed on the selectively emitting material.

As has already been mentioned, it is important that the radiation be confined to a relatively narrow wavelength region, near the absorption edge of the semiconductor material used to fabricate the photovoltaic cell. The degree to which a radiator satisfies this requirement can be expressed quantitatively in terms of the spectral efficiency which is defined as:

$$\eta_{spec} = \frac{\int_0^{\lambda gap} \frac{\lambda H(\lambda)}{hc} E_{gap} \, d\lambda}{\int_0^{\infty} H(\lambda) d\lambda}$$

where

λ = wavelength

λ_{gap} = wavelength of the radiation with energy equal to the photovoltaic cell semiconductor material bandgap

$H(\lambda)$ = spectral irradiance

h = Plancks constant

c = velocity of light

E_{gap} = photovoltaic cell bandgap

The spectral efficiency is a measure of the fraction of the energy emitted by the selective emitter which can be converted by the photovoltaic cell into useful energy, if the photovoltaic cell were 100% efficient in its conversion. Thus, it forms a useful measure of the merit of a particular material as a selective emitter. The central problem of this investigation is to find the material with the highest possible spectral efficiency.

In addition, the radiation intensity should be as high as possible, since the conversion efficiency is a strong function of the incident intensity. Highest conversion efficiencies occur at maximum intensities. As a practical matter it is desirable to have the incident intensity in the 1 to 20 watt cm^{-2} range. Also, practical considerations of the fabrication of a photovoltaic cell require that the cell be fabricated using either germanium or silicon, which have absorption edges at 1.8μM, 1.1 μM respectively. Even silicon is probably not a realistic choice at this time. The reason for this is that, in order to get a match between the spectral characteristics of the emitter and the photovoltaic cell it is necessary to operate at very high temperatures. The higher the energy of semiconductor absorption edge, the higher the required temperature. Thus, it appears that to use a germanium photovoltaic cell requires operation of the selective radiative emitter in the 1400 to 1800°K range, while suitable operation of a corresponding silicon photovoltaic cell would require operation in the 1800 to 2200°K range. Continuous operation at high temperatures presents severe stability problems with respect to the selective emitter, and hence, it is felt that at this time efforts should be devoted toward radiators which are compatable with germanium photovoltaic cells. Thus, it is necessary that the selective emitters which are developed be stable in the 1400 to 1800°K range.

Also, the material must be stable under thermal cycling. A relatively large area emitter is required for most practical applications and this means that it must possess reasonable strength and be capable of being fabricated into simple geometric shapes which are necessary to get the desired heat transfer characteristics from the thermal source to the radiator without having undue mechanical stresses develop.

C. Summary of the Desirable Radiation Properties

1. The spectral efficiency should be as large as possible.
2. The material should have the highest total emissivity, compatable with the requirements of number 1 above. Even though the emissivity is high in a relatively narrow band, because of the fact that it is undesirable to have radiation emitted outside this narrow region, the total emissivity for the body may be quite low.
3. The material should be stable at 1800°K and preferably higher. It should be stable in an air ambient. It is possible that materials which are stable in inert gases would be useful.
4. The material should be able to withstand thermal cycling from room temperature up to the elevated temperatures and back down for a number of cycles.
5. The material should ideally have enough strength to be self-supporting so that thermal losses through the supporting structure can be minimized.
6. The material should have a relatively high thermal conductivity so that there is efficient heat transfer from the surface at which the heat is applied to the surface at which the radiation occurs.

D. Consideration of Possible Materials Candidates

One can make some general statements about the possible classes of materials which will satisfy the conditions summarized above. The high melting temperature and stability requirements, which are mentioned above, immediately rule out many materials. In fact, if one insists on stability at 1800°K and above in an air ambient most materials can be ruled out except for the metal oxides and the noble metals. However, the metals are ruled out because of their extremely broad emission spectra, which is a result of the high concentration of free electrons. Metals of any kind are not appropriate for this application. If one allows for the possibility of using an inert atmosphere, the borides, nitrides, and carbides are also possible candidates. However, a review of the spectral radiative properties of the nitrides, carbides, and borides indicates that they are fairly strong emitters over a wide band of frequencies. In fact some are reasonably gray bodies and so are not suitable even if inert atmospheres are considered. The glasses would appear to be a reasonable class of candidates for at least a host material which was doped with suitable emitting atoms. However, most of the glassy materials, with the possible exception of silicon dioxide, are ruled out by the 1800°K and above, operating temperatures. Thus, there is really only one class of materials which appears to satisfy all of the above requirements-oxide ceramics. Many of the oxide ceramics are stable in air at temperatures well in excess of 1800°K and some of these ceramics do indeed exhibit very low total emissivity at 1800°K and above. One particular class even exhibits selective emission of the sort desired.

The class of materials which appears to best fit the desired selective radiative property is that of the rare earth oxides. Many of the rare earth oxides exhibit a very low total thermal emissivity. They are quite stable at temperatures above 1800°K and in some cases exhibit narrow emission spectra in the appropriate wave length range. While the thermal conductivity of these materials is not as high as might be desired, it appears to be sufficiently high that heat transfer can be kept relatively efficient by using sufficiently thin materials. Little is known about their ability to withstand thermal cycling at this time.

The desire to have a selective emitter is not new. In fact, the existing literature(2) dates back to 1905 when there was considerable interest in developing a selective emitter which could be excited by a kerosene lantern or a gas flame. In that case, the need was to find a material which could be thermally stimulated by kerosene lantern or a gas flame, and, which would have its primary emission characteristics in the visible and hence increase the lighting efficiency of such devices. The common Welsback mantle, which is still in use today, was studied in two papers dating from 1905 and 1918(3). Interestingly but not surprisingly, the rare earth oxides were found to be suitable for this purpose.

There are two rare earth oxides which appear to be particularly promising. These are Er_2O_3 and Yb_2O_3. In the case of Er_2O_3 the match between the radiation spectrum and the absorption characteristics of germanium are quite good and in the case of the Ytterbium oxide a match occurs with silicon. It has been shown by Guazzoni,(4) that the use of Er_2O_3 can lead to a spectral efficiency which is approximately .5 for germanium. This compares with a spectral efficiency of about .35 for an ideal blackbody in the same temperature range. Thus, there is a significant increase in the spectral efficiency when one uses a selective emitter fabricated entirely from the pure rare earth oxides.

III. Method of Attack

The original proposal under which this work was funded called for a three-year program. The first year was to be devoted to the determination of those materials systems which would be most promising as selective emitters, and the construction of measurement equipment which would be suitable for determining the spectral efficiency of materials which were fabricated for this purpose. In accordance with this plan a literature search has been conducted, measurement apparatus has been constructed, initial samples fabricated, and preliminary measurements made during the past year.

The literature search indicated that the most promising materials to pursue for selective thermal emitters were the rare earth oxides. In particular it appears that two rare earth oxides Er_2O_3 and Yb_2O_3 would be the even most promising when used as a mixture. The literature search indicated that significant energy transfer can occur between different rare earth ions, and it appears entirely feasible to transfer energy between ytterbium and erbium rare earth ions, with the resulting emission spectra being highly concentrated near the band gap edge of germanium. Thus, it was decided to concentrate the earliest work on the fabrication and measurement of pure samples of erbium oxide and ytterbium oxides and their mixtures.

The techniques which were used to fabricate these samples are described in Section IV below. Initially, because of the measurement technique which was to be used to measure the hemispherical emissivity and because the geometry was compatible with that which one would expect to use in a thermophotovoltaic system, it was felt that the most desirable sample fabrication technique would be to flame spray the selective emitter on a cylindrical tubular supporting structure. However, as will be described below, difficulties were encountered in the flame spraying. In particular, in the case of erbium oxide, it appeared that a great deal of technological development would be required to get satisfactory flame spray coating, especially in view of the large number of samples and different sample compositions which we expected to encounter in the process of performing this investigation. Thus, the sample geometry was changed so that samples of the selective emitter material were enclosed inside of a heated sample tube such that all that was required were samples which were sintered to the proper dimension. This greatly simplified the sample preparation procedures.

The measurement techniques, which are described below, are the result of considerable analysis. Initially it was felt that the hemispherical emissivity, which is required to determine the total energy emitted, would best be done on the equipment developed by R. Taylor at TPRC. This equipment has been extensively described in publications sited in the references.(5) However, because of the difficulties encountered in the flame spraying of these materials, it was decided to switch to the geometry described in Section VF, so that fabrication of the samples could be eased considerably. The techniques which were developed for measuring the spectral emissivity and the total emissivity of the samples are described in Section V.

IV. Materials and Sample Preparation

A. Flame Spraying

Initial efforts at sample preparation for emissivity measurements were concentrated on flame spraying the desired oxides onto a refractory metal substrate with a Metco Type 5P ThermoSpray Gun purchased from Metco, Inc.* This gun is designed for spraying metal, ceramic and cermet powders using an

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*Metco, Inc., 324 Eisenhower Lane, Lombard, Illinois 60148 oxygen and acetylene flame. The powders are fed into an aspirator chamber through a metering valve by gravity. From here the powder is propelled through the flame where it melts and is deposited on the substrate.

Of the refractory metals, niobium and tantalum were singled out as possible substrate materials for their close correlation of linear thermal expansion coefficient with erbium and ytterbium oxides (Fig. 2 and Fig.3). However, due to difficulty in obtaining suitable niobium tubing, tantalum tubing was used for all work to date. Surface preparation of the substrate is critical to adhesion of the coating, a roughened surface being necessary. Acid etching, sand blasting, and liquid honing were investigated, but blasting the surface with angular steel grit proved to be the most satisfactory method of roughening the tantalum surface prior to flame spraying.

Original studies to determine spraying conditions yielding optimum adhesion and uniformity of coatings were performed with a mixture of rare earth oxides due to its availability and ease of spraying. A Type 5PV Vibrator Unit was used with the ThermoSpray Gun to improve feeding of powders through the metering valve. Also, it was found that more uniform and cohesive coatings were obtained with the use of a Type PSA Air Jet Assembly which introduces a high velocity blast of nitrogen at the tip of the gun. Coating density and uniformity was studied by scanning electron microscopy and was found to be excellent as can be seen from the attached photographs. (Fig. 4) Adhesion of the coatings was studied by thermally cycling the samples to 1600°C in an argon atmosphere. In an effort to increase coating adhesion, an intermediate layer of niobium powder was sprayed onto the substrate prior to application of the oxide coating. However, samples prepared both with and without this intermediate layer performed equally as well under thermal

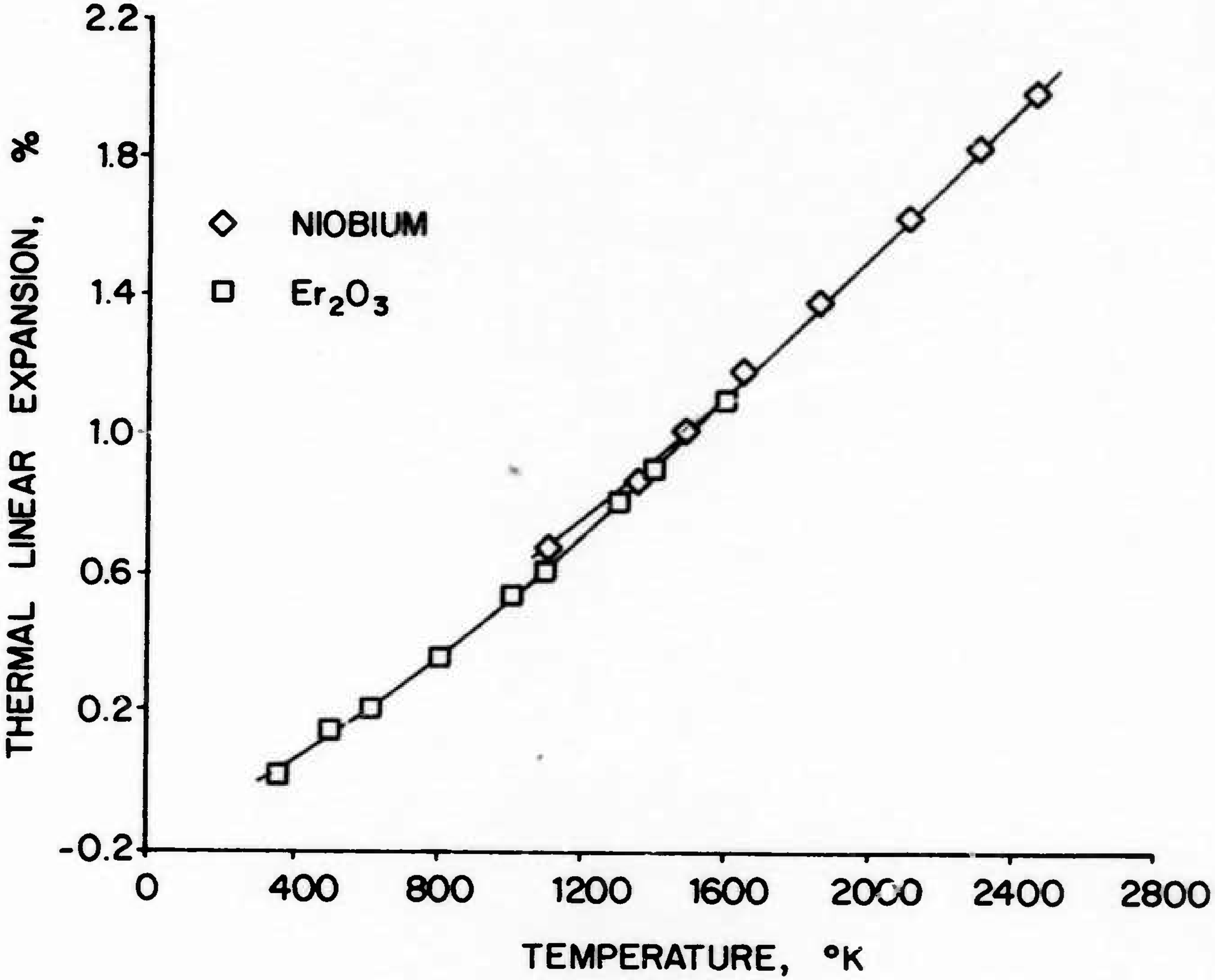

Fig. 2 Temperature Dependence of the Thermal Linear Expansion of Niobium and Erbium Oxide

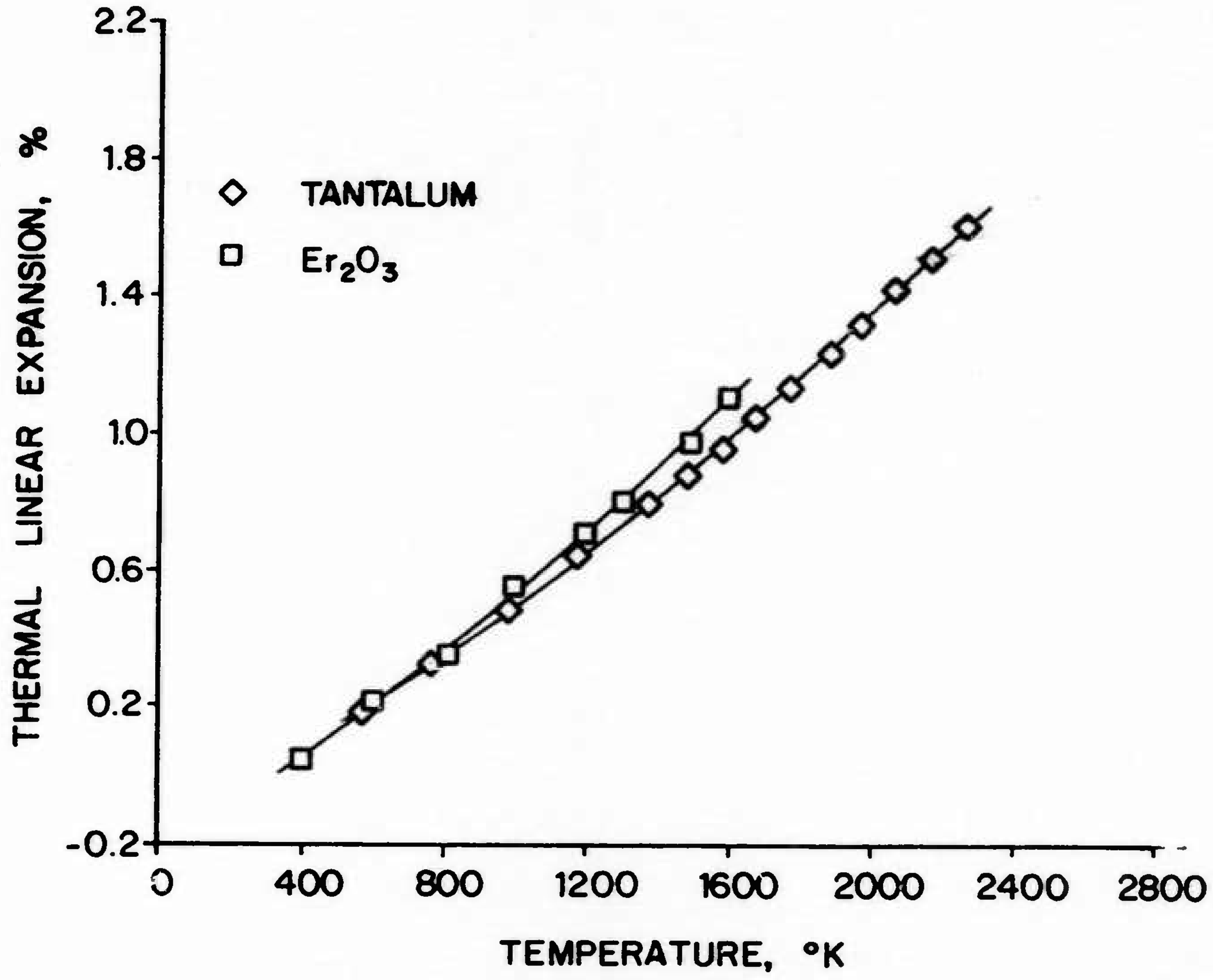

Fig. 3 Temperature Dependence of the Thermal Linear Expansion of Tantilum and Erbium Oxide

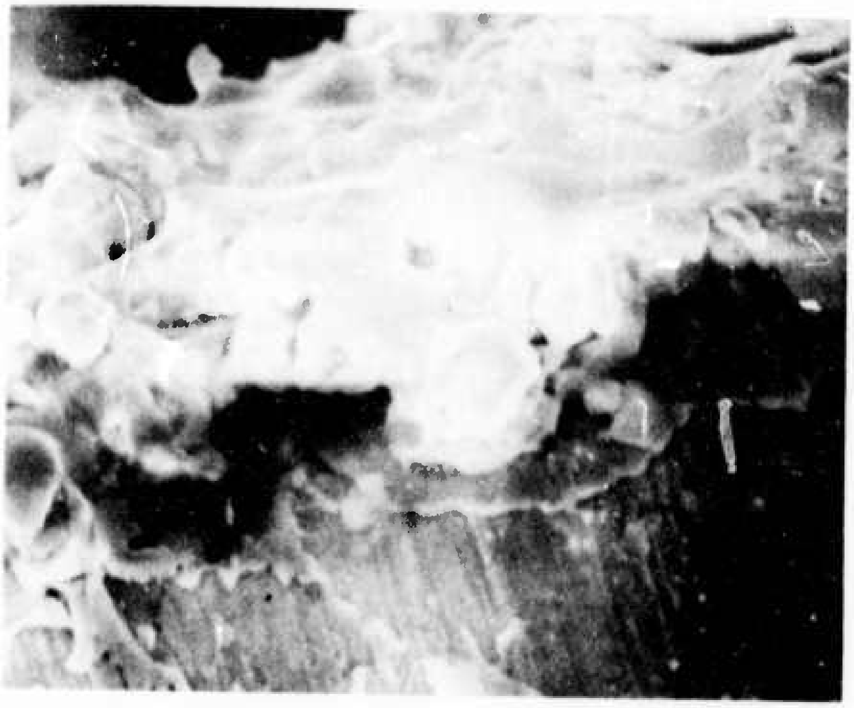

Fig. 4(a) 300 X Side View Showing Rare Earth Oxide Coating (Above) Flame Sprayed Onto Niobium Substrate.

Fig. 4(b) 3000 X of Rare Earth Oxide Coating Flame Sprayed Onto Niobium Substrate.

cycling, showing only slight crazing and remaining well adhered to the substrate.

After determining the spraying conditions which lead to the most desirable coatings, attempts were made to flame spray erbium oxide. Several difficulties were encountered, though, due to difficulties in feeding erbium oxide powders purchased from Ventron, Inc., through the metering valve of the gun. The powders were highly agglomerating and tended to clog in the canister, even with use of the vibrator unit. Attempts to alter the physical properties of the erbium oxide and increase its ease of spraying included calcining the powders at high temperatures (~1000°C) pressing, sintering, and regrinding the oxide powders, and freeze drying. However, the most successful method to data has been via preparation of the hydroxide and subsequent decomposition to yield the oxide.

B. Er_2O_3 Preparation

Preparation of the oxide by the following procedure:

$$Er_2(SO_4)_3(aq) + 6NH_4OH \rightarrow 2Er(OH)_3\downarrow + 3(NH_4)_2SO_4$$

$$2Er(OH)_3 \xrightarrow[24\ hrs.]{800^\circ C} Er_2O_3 + 3\ H_2O$$

appeared to produce less agglomerating, more free flowing powders. Although some improvement in the sprayability of these powders was observed, the feeding was too eratic to produce uniform coatings, and too slow, resulting in overheating and oxidation of the tantalum substrate.

In accordance with the findings of Mazdiyasni and Brown$^{(6)}$ attempts were made to synthesize the isopropoxide by direct reaction of erbium metal with isopropanol. Even with the use of mercuric chloride and mercuric acetate catalysts the reaction failed to go. However, erbium isopropoxide was finally synthesized by the following method:

$$ErCl_3 \cdot 6H_2O + 6SOCl_2 \rightarrow ErCl_3 + 6SO_2\uparrow + 12HCl\uparrow$$

$$ErCl_3 + 3NaOPr^i \rightarrow Er(OPr^i)_3 + 3NaCl\downarrow$$

From this point the procedure of Mazdiyasni and Brown was used to prepare the oxide as follows:

$$Er(OPr^i)_3 + 3H_2O \xrightarrow{\text{benzene}} Er(OH)_3\downarrow + 3Pr^iOH$$

The hydroxide precipitate was washed repeatedly with isopropanol and vacuum dried at 60°C for 20 hours and subsequently calcined at 8[illegible]0°C for 24 hours to produce erbium oxide. This vacuum drying and calcining procedure was also carried out with the hydroxide prepared from the sulfate. This oxide preparation, along with a motorized stirring mechanism mounted in the canister of the gun to help prevent clogging of powders above the metering valve, resulted in improved, but not yet satisfactory spraying of the powders. Also, preparations from both the isopropoxide and the sulfate appeared to result in the same physical properties of the oxide. Continued efforts in this area are planned.

C. <u>Sintering</u>

In the meantime, samples suitable for emissivity measurements are being prepared by insertion of sintered pellets into tantalum tubing rather than flame sprayed coatings on the surface (See Sec.V).Sintered pellets are prepared by isostatically pressing powders to 60,000 psi and heating in air to 1400°C for 96 hours. At present, pellets are pressed in an available die and machined to proper size for insertion into the tantalum tubing. However, shrinkage during sintering under the above conditions was determined to be 2.8%, and a die to produce pellets requiring little or no machining according to this data is being fabricated.

D. Mixed Oxides

In the area of mixed oxide preparation, Gruss and Salomon(7) have reported the preparation of solid solutions of ytterbium and erbium oxides in varying mole percents by a co-precipitation of the hydroxides with ammonium hydroxide from a solution of the oxides in hot 10% HCl and subsequent calcining to yield the oxides. Accordingly, a 10 mole percent solution of erbium oxide in ytterbium oxide has been prepared, pressed and sintered. Also, 10 and 50 mole percent solutions of ytterbium oxide in erbium oxide have been prepared by a co-precipitation of the hydroxides from an aqueous solution of the sulfates, and have been pressed and sintered. These will be examined by x-ray diffraction to insure solid solutions, and subsequent samples of varying mole percent solutions will then be prepared accordingly for emissivity measurements.

V. Measurement Apparatus and Procedures

A. Introduction

The objective of this phase of the program is to measure the appropriate thermal radiative properties needed to evaluate the spectral efficiency. In the subsequent sections these properties are defined and their measurement techniques discussed. Our approach is a three-fold effort. An initial system utilizing the basic components of the final design is constructed and tested to verify the design calculations. After analysis of this system under actual data-taking conditions, any necessary modifications to the final design will be incorporated. The final design will be a dual system allowing the measurement of the radiative properties from the different approaches described in later sections.

The apparatus for the first step has been partially assembled and tested. Certain features have already been evaluated in preliminary experiments and provide confidence in the design.

B. Thermal Radiative Properties Required

In order to determine the spectral efficiency the following two properties are required:

1) Hemispherical Spectral Emittance, $\varepsilon\ (2\pi,\lambda,t)$ for a spectral range of 2.5 to .6 electron volts (.5 to 2.0μm) and temperature range of 1500°K to 2000°K.
2) Hemispherical total emittance, $\varepsilon(2\pi,t)$ for the temperature range of 1500°K to 2000°K.

where

λ = wavelength

t = temperature

The emittance is defined as the ratio of the self exitance* of the specimen to that emitted by a blackbody radiator under the same conditions. "Spectral" means in a small wavelength region; while "total" means over all wavelengths. "Hemispherical" means the value over the entire hemisphere the object is radiating into.

The hemispherical emittance can be measured directly. However, the difficulty in collecting the radiant flux over the entire hemisphere promotes the use of indirect measurements.

The mathematical relationship for the hemispherical emittance is:[8]

For hemispherical Spectral Emittance:

$$\epsilon(2\pi,\lambda,t) = \frac{1}{\pi} \int_{\text{hemisphere}} \epsilon(\theta,\lambda,t)\,d\Omega$$

For hemispherical Total Emittance:

$$\epsilon(2\pi,t) = \frac{1}{\pi} \int_{\text{hemisphere}} \int_{\substack{\text{Spectral}\\ \text{Range}}} \epsilon(\theta,\lambda,t)\,d\Omega\,d\lambda$$

or

$$\epsilon(2\pi,t) = \frac{1}{\pi} \int_{\substack{\text{Spectral}\\ \text{Range}}} \epsilon(2\pi,\lambda,t)\,d\lambda$$

Where $\epsilon(\theta,\lambda,t)$ is the emittance in the direction θ at temp. t and wavelength λ. This directional emittance can easily be measured. For most dielectric materials the directional emittance is reasonably constant.

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*Flux per unit area leaving the surface; the modifier "self" means due to emission only, excludes reflection.

This allows removal of the directional dependence from the emissivity formulas. A detailed study of this relationship(9) shows that hemispherical emittance is directly related to their normal emittance and is within 5% of it, as illustrated in TPRC Vol. 7, p. 24a.(8) The measurement of normal emissivity provides a suitable alternate to the direct measurement of hemispherical emissivity.

The total hemispherical emissivity can be obtained by implicit integration over λ by utilizing a detector that responds to the wavelength range of integration or by numerical integration of the spectral emittance. Either method can be used can be utilized and would serve as a check of the correct value.

C. Measurement Methods

Even though only normal emissivities will be measured, there still is a variation in the parameters of the measurement. All materials will be viewed perpendicular to their surface (i.e., normal); only a small wavelength range will be considered at any one time; and only the energy in a finite solid angle will be measured. However, there is no standard convention as to the value of these parameters to constitute a normal spectral emittance measurement. For most materials the emittance is a slowly varying function of both temperature and viewing angle.(10) This allows reasonable comparison of measurements taken with instruments of different geometries. However, the purpose of this research is to directly compare materials, and, as such the geometry must remain identical for every sample to insure accurate comparison. The spectral bandwidth of our instrument varies from about 50 Å (.024 ev), in the visible, to about 150 Å (.0095 ev) at about 1.4 μm (.88 ev). Radiant flux is collected over a cone of approximately 13° (.0357 steradians).

Various investigators have constructed instruments for normal spectral emittance measurements and much of their findings can be applied directly.(10,11,12,13) Our approach differs from previous methods in two respects: (1) It is designed for computer control of the experiment and data processing and, (2) variable spectral resolution is planned while maintaining the same sample area viewed. The utilization of computer control will allow large amounts of data to be taken very quickly and accurately. It is especially important to take all data under identical conditions and to minimize the effects of thermal drift of the sample and drift in the electronics. Computer control provides the best possible solution. The control of the spectral resolution is important to insure the correct integration of the spectral emissivity curve. For a material with narrow spectral bands as the rare earth oxides will have, the measured width of the bands is a direct function of the spectral resolution of the instrument and hence the area under the curve is, therefore, a function of the instrument's resolution. Care must be exercised to provide that the same size area of the sample is viewed in each case to remove the possibility of surface granularity affecting the results. This restriction is not met by several of the instruments previously referenced(14) and care must be exercised when examining their results.

The basic measurement technique used is a direct ratio method. The sample and a reference blackbody are measured under identical conditions and the values ratioed. This technique removes the usual corrections necessary for mirror reflectances, window losses, and atmospheric absorption. The key to the method lies in maintaining identical conditions, particularly temperature. A temperature difference between the sample and the reference of only 1° at 1500K will cause an emissivity error from 1/2 to 2%, depending on the wavelength being measured. Because of this critical temperature dependence, the blackbody and sample are constructed together and heated identically. The points where data is to be taken are as close together as physically possible to further reduce thermal gradient affects. The sample geometry used to accomplish this is described in section VF.

In order to correctly ratio the two signals any bias or background noise must be subtracted first. This background level is a function of the same variables that affect the emissivity measurement and can only be found by measurement under actual experimental conditions. The background level is measured by looking just off to one side of the sample at a background reference. This background level can be sampled at any time by the computer.

The ability to take data from the sample, the blackbody reference, and the background reference is provided by the oscillating mirror shown in Figs.5,6. This mirrow allows data collection from four different distinct spots in the vacuum system utilizing exactly the same optical system. All optical components are the same. All abberations are the same. And, most important, the spectral resolution and spectral bandwidth are the same. The system may be operated to take reference readings off to one side of each point or on each side of the heating tube midway between the data points.

D. Optical Systems

Two optical systems are currently under investigation. One would provide maximum throughput and thereby allow lower temperature and extreme wavelength range measurements. The other would provide controllable resolution while maintaining all other factors constant. The advantage of the first system, shown in Fig. 5, is that it is optically the simplist system and a prototype has already been constructed. The second system shown in Fig. 6, is optically more complex and requires physically more

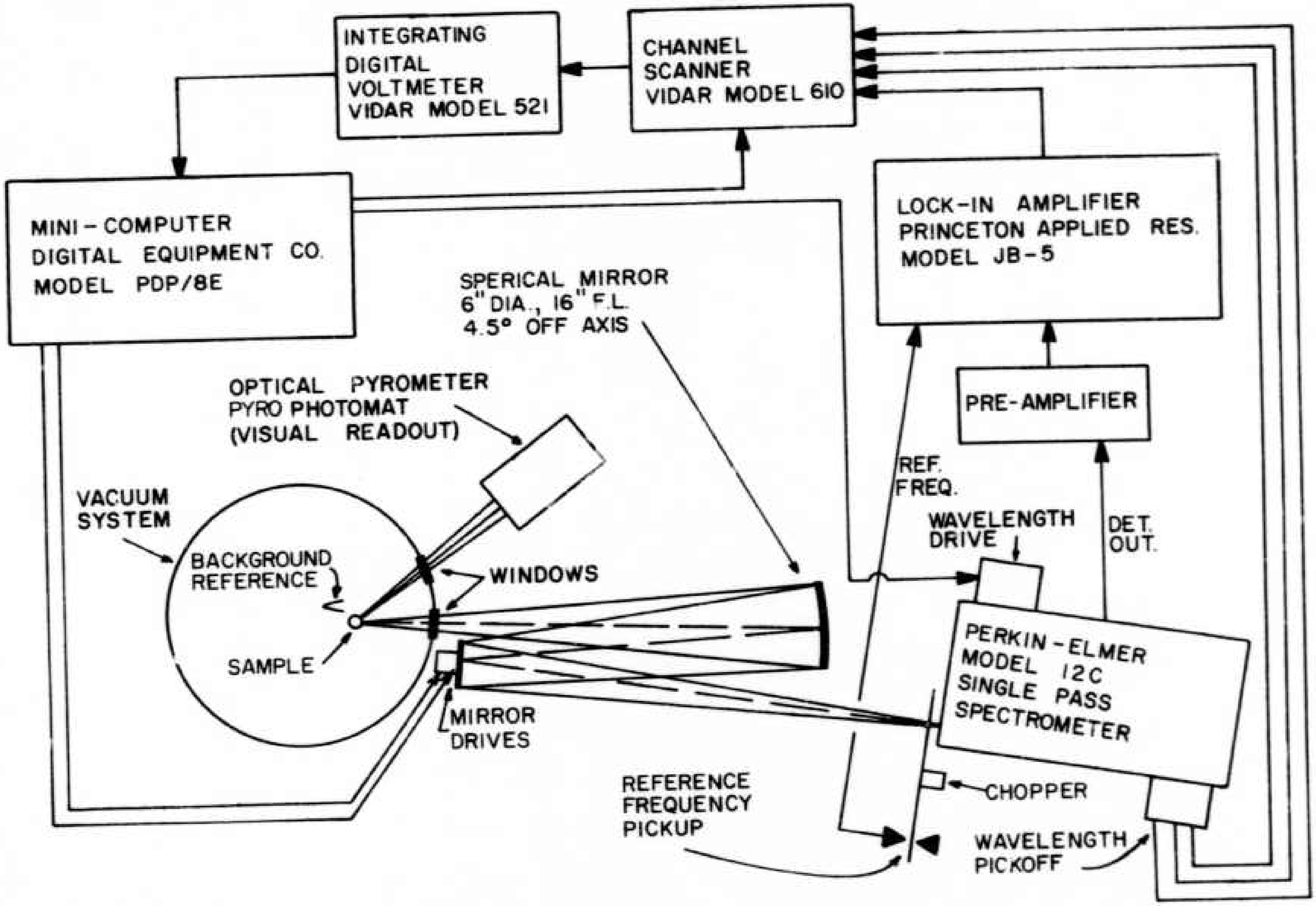

Fig. 5 Maximum Throughput Optical System

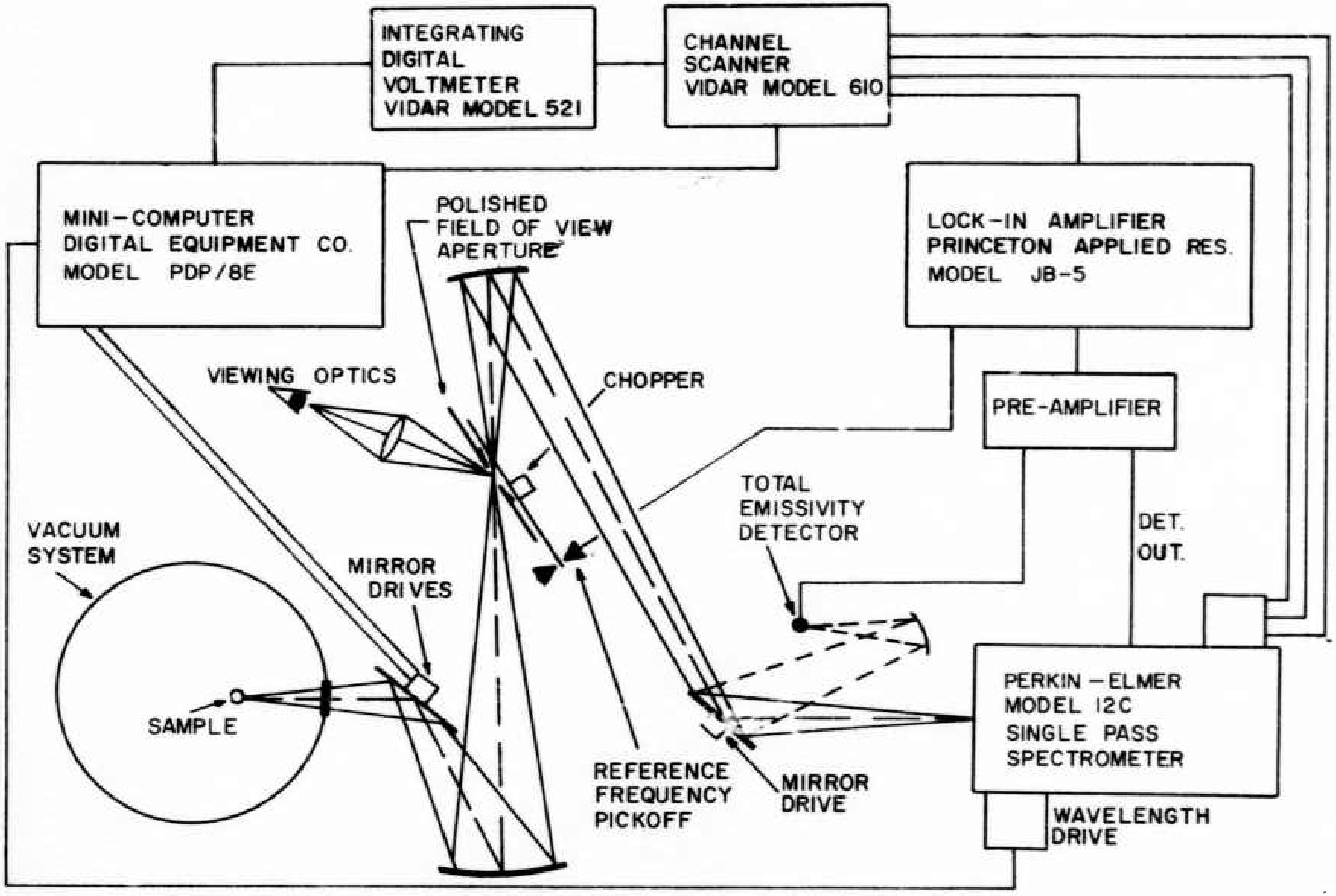

Fig. 6 Controllable Resolution Optical System

room to house it. It has the advantage that by controlling the resolution, the width of spectral spikes are controlled and thereby the areas under those spikes are controlled. If the resolution is adjusted to a constant value in energy units, not wavelength, then the area under any two spikes of equal energy will indeed be the same. This factor becomes quite important when the spectral spike approaches the resolution limit.

In both systems the entire cone of light which escapes the vacuum system window is collected. Only first surface mirrors are used to allow transmission of the complete spectral range and a Perkin & Elmer prism single pass monochrometer is used. A frequency tracking amplifier locks onto the chopping frequency and amplifies the signal for the integrating voltmeter. Integration time is chosen to remove noise yet still allow for rapid data taking.

E. Preliminary Experiments

The prototype system shown in Fig. 5 has been constructed. It was calibrated through the use of a mercury arc lamp whose spectral output was checked by the Purdue Physics Department Spectroscopy Group by their Humphrey Scanning IR grating spectrometer with a Corning 3-66 filter, a Wilson Amp, and a 100 μ slit.

The prototype system has been successfully integrated with the PDP-8 mini computer and several data runs have been successfully executed. Absolute flux measurements were made using a calibrated tungsten strip lamp whose temperature was accurately known and the systems throughput was within the expected tolerance. Resolution as measured with the mercury arc lamp was also within expectations. Computer control of the scanning mirror has proved to be very accurate and repeatable.

Modifications to the computer are currently underway to allow simultaneous testing of the wavelength drive, scanning mirror control, and data taking systems. It is hoped to have analysis of the preliminary system completed in the next few weeks allowing the total effort on the construction of the final optical system.

F. Multiproperty Apparatus

Samples were prepared in the form of thin walled tantalum tubes to fit the multi-property apparatus at the Thermophysical Properties Research Center. Figure 7 is a photograph of this system which is described in detail in reference 5. The sample is suspended vertically in a vacuum system with a water cooled bell jar. Regulated power supplies can provide over 10 KW of power to directly heat the tantalum tube, by passing a current through it. Since the sample holders at the ends of the tube are cooled, a temperature profile with a maximum at the middle of the sample is created. If the tube is long enough (6-8 inches), the second derivative of temperature with respect to distance along the tube will also be zero at this point. That is, all the heat produced by the electric current will be reradiated, none will be conducted along the tube, and the temperature is constant for a short distance along the tube.

A 0.40 inch diameter hole drilled in the tube will provide a blackbody reference, and the sample material will either be flame sprayed onto the outside of the tube, or sintered into a pellet placed inside the tube with another .040 inch hole to allow its surface to be visible. The two sample geometries are shown in Fig. 8. One sample material plug insures that the blackbody cavity will be at a uniform temperature, the other preserves the symmetry of the sample.

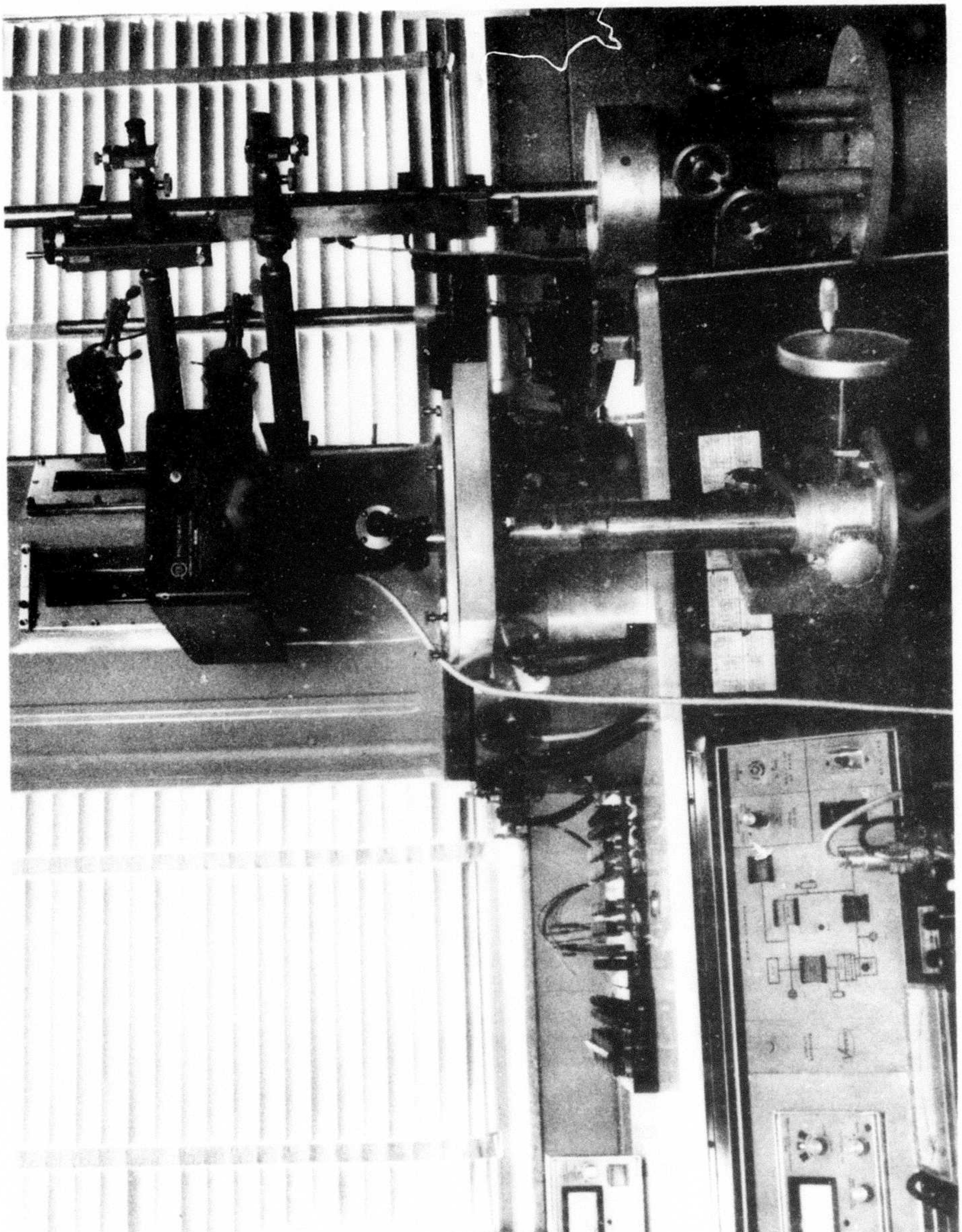

Fig. 7 Multiproperty Measurement Apparatus

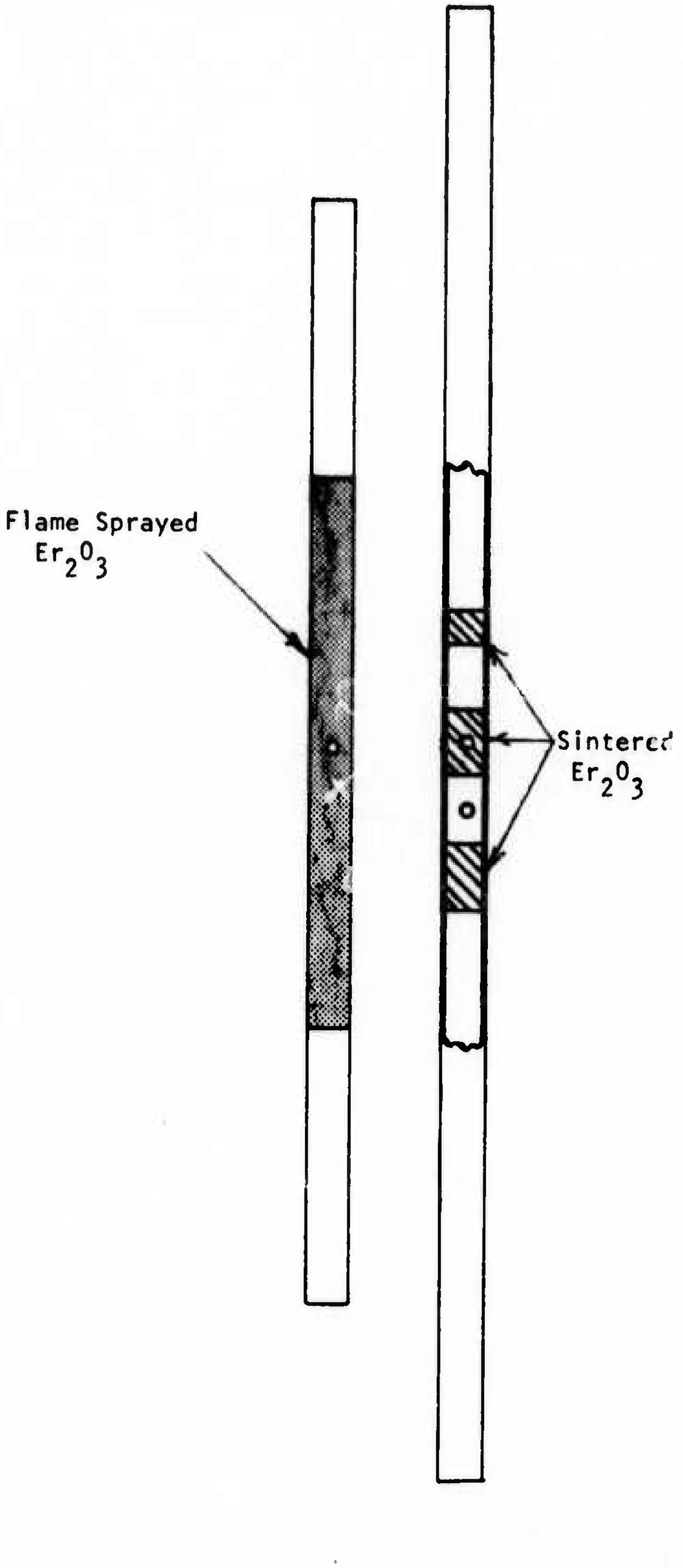

Fig. 8 Sample Geometries

For the flame-sprayed samples, the total hemispherical emissivity can be calculated by measuring the power supplied to the middle part of the tube (voltage probes are placed about one inch apart), and dividing it by the power that a blackbody of the same area, and same temperature (measured with an optical pyrometer focused on the blackbody hole) would radiate.

For the sample with sintered pellets inside the tube, another method must be used since most of the exterior surface of the sample is tantalum. The spectral emissivity will be integrated over the range of wavelengths where there is significant energy (.5-20μ), as described in section VD.

G. Data Collection and Processing

A PDP-8E computer with a disk operating system, graphics display and hardcopy unit, high speed paper tape units, integrating digital voltmeter and 100 channel scanner is available to control, collect, and process data. A block diagram of this data acquisition system is shown in Fig. 9. The numbers in the PDP-8 and the disk blocks give the number of words of memory for each of these devices. The program switches provide 115 volts AC outputs to control drive motors and mirror switching solenoids.

A program has been written to control the wavelength drive of the spectrometer, with the option of taking data as the wavelength is scanned continuously, or halting the drive while each data point is taken. Appendix 1 is a copy of this program. The computer senses the position of the wavelength drive by measuring the voltage across a ten-turn potentiometer that is coupled directly to the drive shaft. A calibration routine converts this voltage to the energy in electron-volts of photons of this

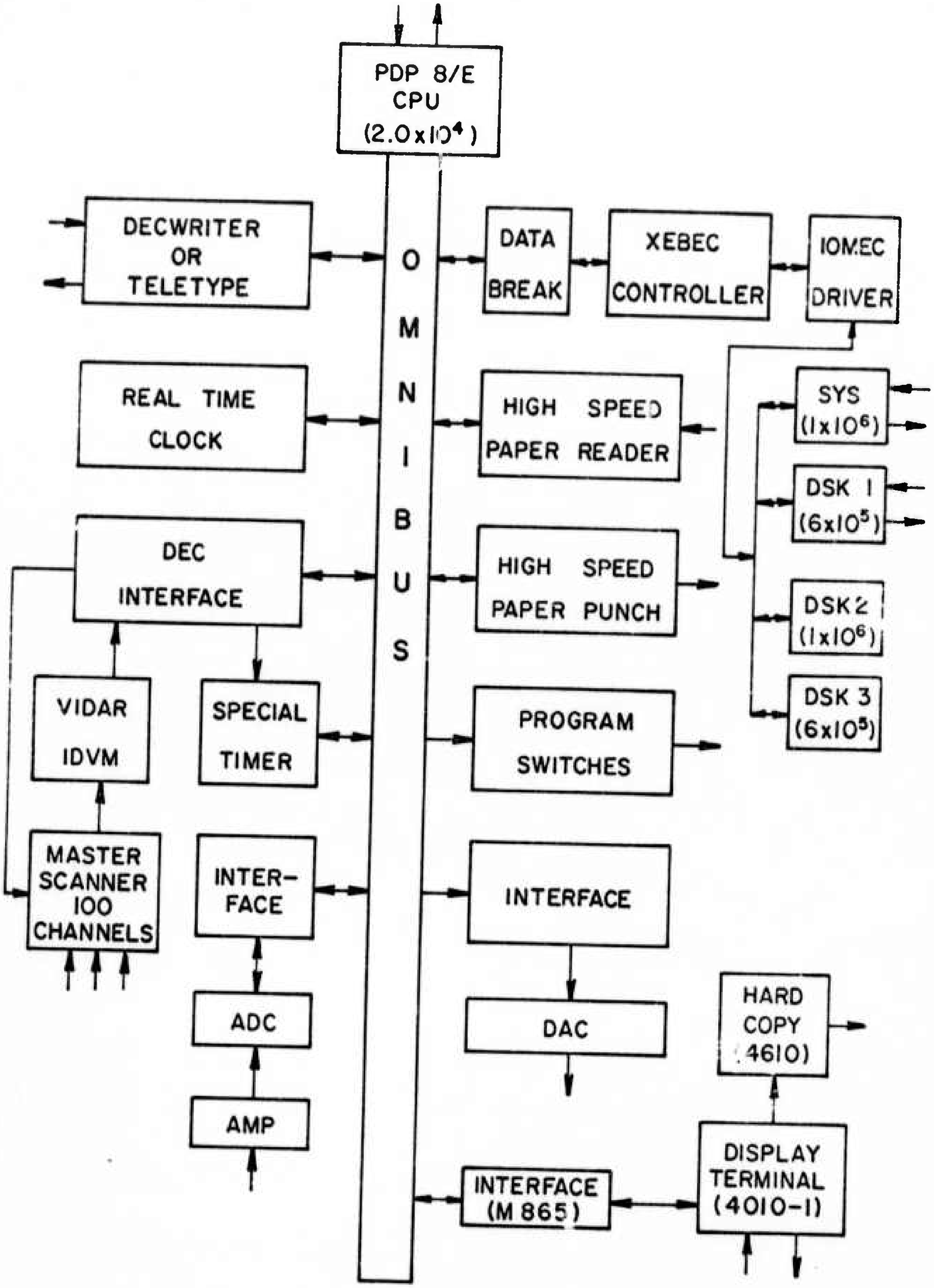

Figure 9. PRL Digital Data Acquisition System (Block Diagram)

wavelength. An energy scale is used so that integrations performed to calculate the spectral efficiency will correspond directly to areas under the curve that is plotted here. Figure 10 is a typical example of the computer plots which are generated.

The program switches that control the wavelength drive motor and mirror switching solenoids are set with assembly language instructions that are inserted directly into the Fortran II Program. These SABR instructions are denoted by an S in column 1. The spectral emissivity is calculated by comparing the sample data with the blackbody data, and then stored in a data file on the disk and plotted on the graphics display in real time.

Another program reads the data file from the disk, calculates the spectral efficiency, and compresses the data for permanent storage on another disk and paper tape.

VI. Results

In Fig. 10 we show the computer output of a preliminary run which was made on a sintered erbium oxide sample operated at 1800°K. In Fig. 10 the computed emissivity of the erbium oxide at 1800°C is plotted.

This curve represents preliminary data and the state of the measurement apparatus at the time of the writing of this report. There are a number of comments which can be made with regard to this data. First, there appears to be a systematic error leading to a measured emissivity which is higher than it should be at the high energy end of the range. This is confirmed by a separate run which was made on a tantalum sample where there is reliable published data available. Second, additional work will need to be done to ensure that the spacial resolution of the system is such that we are observing only the Er_2O_3 and only the blackbody cavity when appropriate.

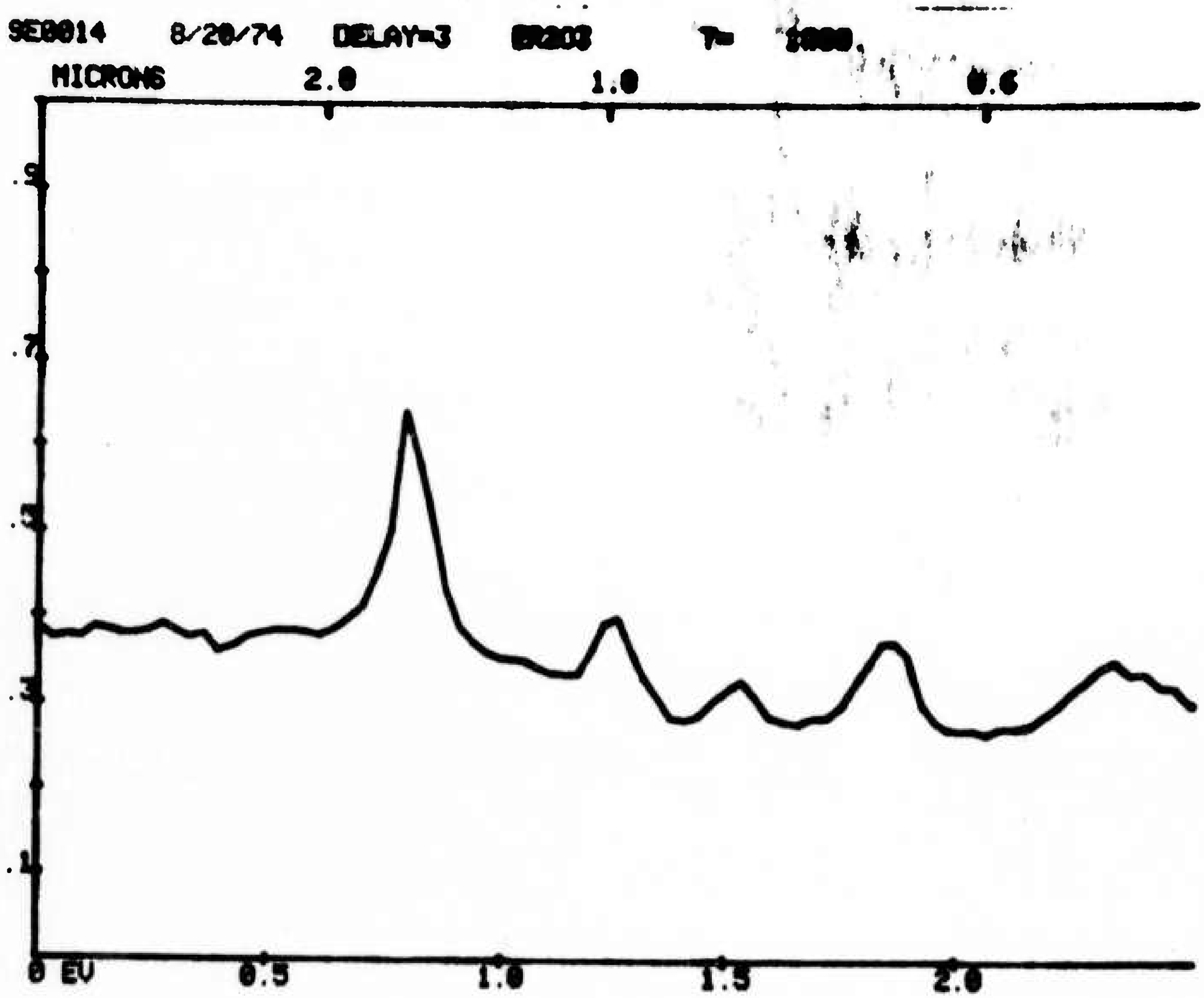

Fig. 10 Emissivity of Erbium Oxide at 1800°K. Preliminary data-useful range, .5 ev to 2.0 ev; zero corrections not made; systematic errors evident, but not evaluated.

Both of these difficulties are in the process of being corrected and it is expected that they will be corrected within the next few weeks.

VII. Conclusions

The goals which were set up in the original proposal for the first year of work have been met, namely, that initial samples of promising selective emitters be prepared and that a measurement system capable of making rapid and accurate measurements be fabricated and tested. While the optical system which has been developed will need some further refining with regard to the spacial resolution and calibration, it is expected that this work can be completed very shortly and that the measurement system will be operable within four to six weeks.

It has been demonstrated that suitable samples of earth oxides in both pure and mixed form can be prepared. Such samples are presently awaiting measurement and evaluation. It is expected that during the coming year we can make significant progress toward the attainment of a selective emitter which has a spectral efficiency significantly higher than any now presently available.

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Appendix I

```
C     SEE -- TAKES, CALIBRATES, PLOTS EXPERIMENTAL DATA
C
      DIMENSION CAL(9)
      CAL(1)=3.9
      CAL(2)=3.59
      CAL(3)=3.22
      CAL(4)=2.84
      CAL(5)=2.49
      CAL(6)=1.9
      CAL(7)=1.3
      CAL(8)=0.7
      CAL(9)=0.1
      BLANK='      '
C              GET INITIAL INFORMATION
      CALL DATE(MON,IDAY,IY)
1     CALL ERASE
      READ(1,69)FN,DE,EP,LD
69    FORMAT(' ENTER FILE NAME 'A6/' ENERGY INCREMENT 'F4.2/
     1' STARTING ENERGY 'F3.1/' DELAY AT DATA POINTS 'I1)
      READ(1,65)ANOTE,BNOTE
65    FORMAT(' NOTES ',A6/' RETURN TO START TAKING DATA 'A6)
      IF(FN-BLANK)3,2,3
2     FN='SE0000'
3     CALL ERASE
      WRITE(1,14)FN,MON,IDAY,IY,LD,ANOTE
      WRITE(1,66)
66    FORMAT(/'0 EV')
      ICH=72
      IPCH=71
      IRCH=70
      X1=2000
      ISS=0
C              DRAW AXES AND LABEL
      CALL BASE(0.,0.)
      DO 7 L=1,8
      YL=100.*FLOAT(L-1)
      CALL VECT(0.,YL)
      CALL VECT(11.,YL)
7     CALL BASE(0.,YL)
      DO 9 L=1,4
      XL=FLOAT(L)*250
      CALL VECT(XL,700.)
      CALL VECT(XL,690.)
      CALL ABASE(XL,700.)
      WRITE(1,69)L
69    FORMAT(I1)
      CALL GRAPH
```

```
  9     CALL BASE(XL,700.)
C               OPEN A DATA FILE ON THE DISK
        CALL OOPEN('DSK1',FN)
        WRITE(4,14)FN,MON,IDAY,IY,LD,ANOTE
 14     FORMAT(A6,I5'/'I2'/'I2,'DELAY='I1,4X,A6)
C
C               MEASURE WL REFERENCE VOLTAGE
 22     CALL IDVM(IRCH,4,3,REF)
        IF(.1-(REF-3.)**2)23,24,24
 23     WRITE(3,4)REF
  4     FORMAT('CHECK WAVELENGTH REFERENCE ='F9.3)
        READ(1,69)K
        REF=3.
        IF(K-1)22,24,25
 24     EP=EP-DE
        IF(EP-1.)111,25,25
C               DETERMINE PRESENT WL POSITION
 25     CALL IDVM(IRCH,4,3,PPP)
        J=10.*PPP/REF
        R=10.*PPP/REF - FLOAT(J)
        E=CAL(J+1)-R*(CAL(J+1)-CAL(J+2))
        IE=(E-EP)*100.+1.9
C               DECIDE TO TAKE DATA
        IF(IE-1)24,27,75
 27     IF(LD)40,40,29
C               STOP DRIVE MOTOR
 29     CONTINUE
S               CLA
S               6365
        CALL DELAY(4,LD)
C               TAKE DATA
 30     CALL IDVM(IRCH,4,3,REF)
        CALL IDVM(IRCH,4,3,PPP)
        CALL IDVM(ICH,4,3,C3)
C               SWITCH MIRROR
S               CLA
S               TAD (4
S               6365
S               CLA
        ISS=0
        C1=PPP/REF
        J=C1*10
        R=10.*C1-FLOAT(J)
        J=J+1
        E=CAL(J)-R*(CAL(J)-CAL(J+1))
        CALL DELAY(4,1)
C               TAKE DATA
 40     CALL IDVM(ICH,4,3,C2)
C               RESTART DRIVE MOTOR OR SWITCH MIRROR
S               CLA
S               TAD (10
S               TAD \ISS
S               6365
S               CLA
C               WRITE IN DATA FILE
        WRITE(4,44)E,C2,C3
 44     FORMAT(3F9.4)
C               PLOT DATA ON GRAPHICS DISPLAY
        IF(ISS)45,50,45
 45     X=E*250
        Y=1000.*C2/C3
        IF((X-X1)**2-400.)49,48,49
 48     CALL ADOT(X,Y)
 49     CALL VECT(X,Y)
        X1=X
 50     C3=C2
```

```
        ISS=IABS(ISS-4)
C                SENSE FRONT PANEL SWITCHES
   55   IF(IRDSW(0))22,111,59
C                STOP DRIVE MOTOR
   59   CONTINUE
S                CLA
S                6265
        GO TO 55
C                RUN DRIVE MOTOR
   75   CONTINUE
S                CLA
S                TAD (10
S                6265
S                CLA
        GO TO 25
C                END DATA FILE, STOP MOTOR
  111   W=-11
        WRITE(4,44)W,W
S                CLA
S                6265
        CALL OCLOSE
        READ(1,44)W
        GO TO 1
        END
```