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Electret microphone for use in photoacoustic spectrometer and photoacoustic spectrum of some rare earth oxide powders

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Abstract. We describe a new method for the polarization of an electret foil which has proved very convenient and yields a foil having very good performance in a microphone. The variations in the charge accumulation on the electret foil and its decay with time as well as the variation of the microphone sensitivity with different microphone parameters *e.g.* different thicknesses of the electret foil, different back plates and different polarization techniques has been investigated. The sensitivity of the home-made microphone is estimated as 1 mV/μbar. The working of this type of microphone and its comparison with a commercial microphone as used in a (laboratory made) single beam photoacoustic spectrometer is discussed.

A brief description of the photoacoustic spectrometer including microphone biasing and the photoacoustic cell is given. The photoacoustic spectra of some rare earth oxides in the form of powders have been recorded. It is seen that the atomic levels of triplyionized rare earths which are not fluorescent appear very prominently in the photoacoustic spectrum. The spectra for terbium and praseodymium oxides do not show clear peaks probably due to the presence of different stoichiometric forms.

Keywords. Photoacoustic spectroscopy; electret microphone; polarization; rare earth oxides; photoacoustic spectrometer.

1. Introduction

The photoacoustic effect has been used to study the relaxation processes in gases, liquids and solid samples by several workers (Luft 1943; Veingerov 1945; Harshbarger and Robin 1973; Rosencwaig 1973). These studies have emphasized the similarity of the photoacoustic spectrum with the optical absorption spectrum and have identified a number of other potential applications of this method (Kirkbright 1978; Rosencwaig 1978; Ganguly and Rao 1981). Various types of experimental set-up have been described in the literature (McClelland and Kniseley 1976; Adams *et al* 1976; Gray *et al* 1977; Rai *et al* 1981).

The photoacoustic cell used for the generation of the acoustic signal and the electret microphone used for the detection of this signal constitute two very vital components of any photoacoustic spectrometer. In our instrument described earlier (Rai *et al* 1981 only the fixed wavelength version was described) we have used a cell patterned after the earlier work of Kirkbright and have used an electret microphone. The cell described in the present paper has the advantage of a very small volume and has been designed to minimise the effect of scattered light.

The electret microphone has several advantages over a condenser microphone, for example it does not need any biasing voltage, has a low output impedance coupled

with high capacity and can be operated over a wide range of temperature and humidity conditions. Many workers have successfully designed and fabricated sensitive electret microphones for use in photoacoustic spectroscopy (Sessler and West 1964, 1966; Colles *et al* 1979; Rai *et al* 1981). For successful use in an electret microphone the electret foil must be polarised in a permanent manner without introducing any non-uniformities on the electret surface.

In the present paper we describe in some detail the preparation of electret foils for use in a sensitive microphone and discuss the working characteristics of such a microphone.

After a very brief description of the experimental set-up emphasizing the constructional details of the photoacoustic cell we also describe our observations on the photoacoustic spectrum of some rare earth oxides in the powder form. The observed peaks in the PAS have been correlated with the states of the triply-ionized rare earth ions. Previous studies of the optical spectra of rare earth oxides in the solid phase, have reported prominent features in the visible region (White 1967; Dieke 1978; Haensel *et al* 1970; Warenkessel *et al* 1969; Guazzoni 1972).

2. Electret microphone and its characteristics

2.1 *Polarization of the electret foil*

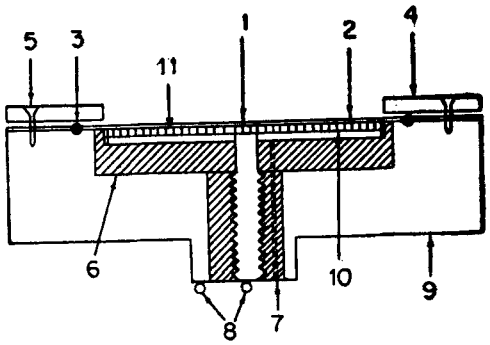
We have used mylar films (Polyster Film Corpn., Delhi) coated on one side either with aluminium or silver, and thicknesses ranging from 7·5 to 25μm. Very thin metallic coating was achieved on one side of the film using vacuum evaporation technique. The coated electret foil is placed on a backing plate of suitable design (as described later) so that the metal coated surface is not in contact with the backing plate. In this configuration the system behaves as a parallel plate condenser with a thin air film and a dielectric slab (the mylar film) between the back plate and the metallic surface.

Two different techniques were used for polarizing the electret foil. In the first method the coated electret film was placed between two metallic plates separated by about 3 mm and a constant D.C. voltage of 3 kV was applied while the whole assembly was kept at an elevated constant temperature of 130°C for 30 min. The temperature was then slowly decreased to the room temperature while the applied voltage was kept unchanged. We refer to this method of polarizing as the " permanent polarization technique " (Sessler and West 1964, 1966; Rai *et al* 1981). In the second method the electret foil was mounted in the microphone as shown in figure 1 and a constant DC voltage of 600 V was applied between the backing plate and the metallized surface at room temperature for 30 minutes. We call this method as " temporary polarization technique."

All the experiments mentioned here were carried out with microphones containing temporarily polarised type of electret foil unless otherwise stated.

2.2 *Performance of the electret microphone*

Figure 2 shows the variation of the microphone signal with the polarizing voltage (for each voltage a new foil was used) changing from 100 to 600 volts DC. The en-



1. Electret diaphragm
2. Brass back plate
3. o-ring
4. Brass ring
5. Screw
6. Teflon insulation
7. Air passage
8. Electrodes
9. Body of microphone (brass)
10. Space filled with air
11. Air layer (between diaphragm and back plate)

Figure 1. Cross-sectional view of electret microphone.

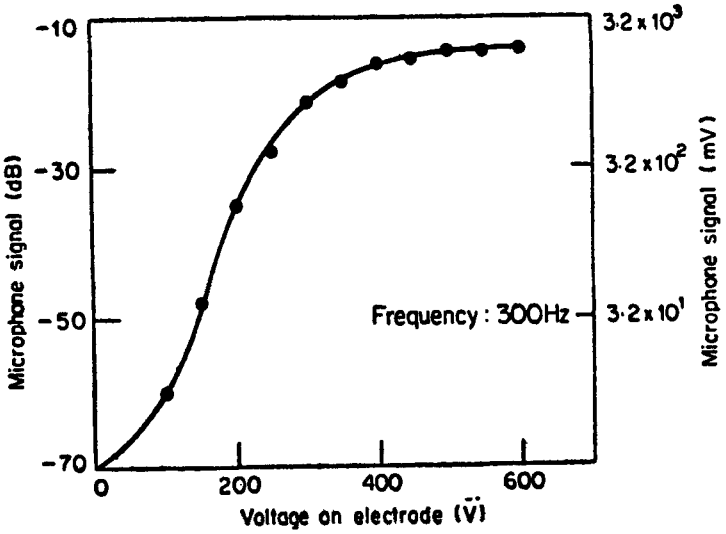


Figure 2. Effect of polarization voltage on the sensitivity of the microphone.

hancement of the microphone signal with increasing polarizing voltage is interpreted as being due to the increase in charge migration to the surface of the electret film. The sensitivity of an electret microphone is expressed as

$$\rho = 4\pi qt' s/(t + \epsilon d) p; \tag{1}$$

here q is the charge accumulated on the surfaces of the foil due to the applied field and t' is the separation between the two charged surfaces of the foil. s is the thickness of the air cushion *i.e.* the ridge height in the back plate, t and d are respectively the thicknesses of the mylar foil and the air gap. ϵ is the dielectric constant of electret foil and p is the atmospheric pressure. Since the electrical capacity of the microphone remains unchanged*, the surface charge in equation (1) is expected to vary

*This may not be exactly true as minor variations in thickness of different mylar foils used in different cases may not be completely ignored. It is however, expected that this variation will not be large.

linearly with the polarizing voltage. This is seen to be true in both the polarization techniques. It is found that in the cases of foils polarized by the temporary polarization technique with applied voltages in excess of 400 volts, saturation of the microphone signal occurs and no increase in signal strength takes place for any further increase in the polarizing voltage. This voltage is equivalent to an electric field of the order of 10^5 V/cm for our experimental set-up.

2.3 *Decay of the microphone sensitivity with time*

The sensitivity of microphones constructed using polarized electret foils is seen to decrease with time. This is essentially due to the decay of the surface charges on the foil and hence can probably be correlated with the electrical conductivity, of the foil material, which is a function of the foil temperature. Thus,

$$\sigma = \sigma_0 \exp(-E/kT), \tag{2}$$

where σ_0 is the conductivity at absolute zero. σ is the conductivity at temperature T, E is the activation energy and k is the Boltzmann constant. The temperature dependence of the conductivity can be neeglected if E is very much larger than kT. Under such circumstances the tiiue constant for the decay of the surface charge can be written as

$$\tau = RC, \tag{3}$$

where R is the resistance of the foil and C is the capacitance of the parallel plate condenser formed by the two charged surfaces and the foil as dielectric.

The time constant calculated from (3) comes out to be 7 months whereas experimental studies indicate a value of $\simeq$ 8 months. We have taken $R = 10^{20}$ ohm/cm as suggested by the Polyster Film Corporation and the capacity of the microphone has been $143{\cdot}0 \times 10^{-12}$ Farad. Figure 3 shows the variation of the microphone sensitivity with time (after polarization). We find that in the case of temporary

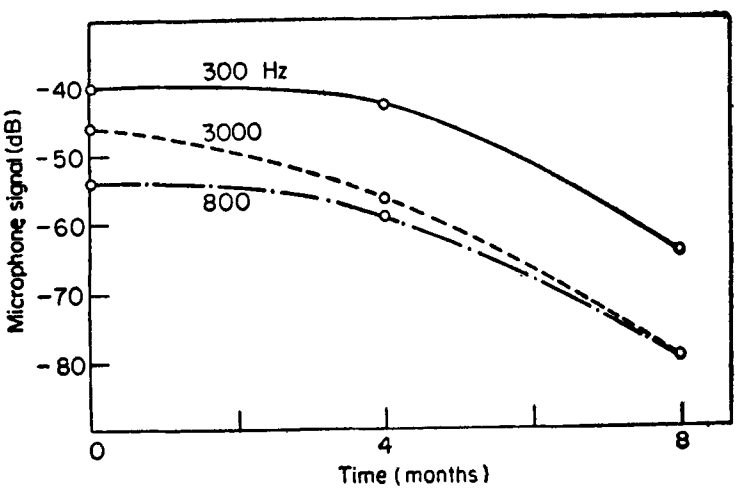


Figure 3. Microphone sensitivity decay with time.

polarization the sensitivity remains nearly constant for 4 months but then rapidly decreases. Table 1 also confirms that the calculated relative sensitivity remains almost constant for 4 months and then decreases. It was shown previously that in the foil polarized by the permanent polarization the microphone sensitivity remains constant upto 14 months and then decreases exponentially (Sessler and West 1966).

2.4 *Dependence of microphone sensitivity on the thickness of the electret film*

Figure 4 shows the variation in the sensitivity of the electret microphone with frequency for diaphragms made of mylar films of different thicknesses. It is found that with decrease in the thickness of the electret film there is an improvement in the sensitivity of the microphone at all frequencies. This is in good agreement with an expression given earlier (Callis *et al* 1969) for a condenser microphone. According to Callis

$$V_{sig} = V_0 (\delta x/x) \exp(-t/RC), \tag{4}$$

$$[\delta C/C = \delta x/x].$$

V_{sig} is the microphone signal, V_0 is the polarizing voltage, δx is the small change in the diaphragm position while x is the separation between the plates (electrodes) of the condenser or in other words is the thickness of the foil. RC is the time constant of the circuit.

Equation (4) indicates clearly that as the electret thickness decreases *i.e.* x decreases V_{sig} *i.e.* microphone signal increases.

Table 1. Relative change in sensitivity with time after polarization.

Time after polarization (temporary) in months	2	3	4	5	6	7
Relative change in sensitivity $\frac{\Delta\rho\bullet}{\rho}$	0·04	0·05	0·05	0·07	0·1	0·09

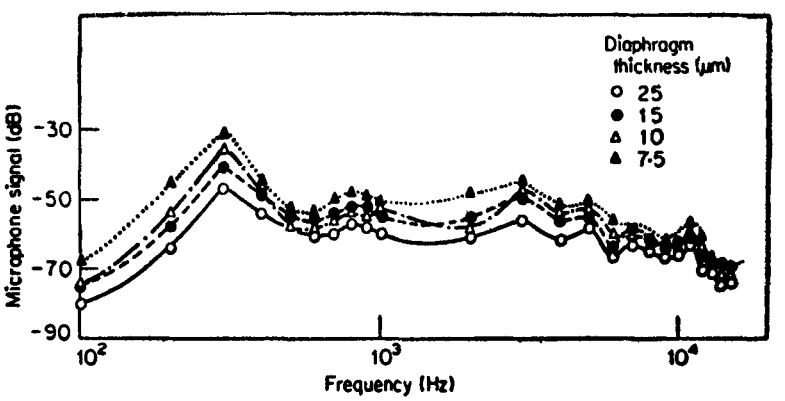


Figure 4. Frequency response of microphone with different thickness of diaphragm.

2.5 *Effect of back plate on microphone performance*

We have used several different types of back plate arrangements in our microphone. Thus, in microphone No. 1, we have used a back plate having four ridges and 180 holes, whereas in microphone No. 2 the back plate has only two ridges and 26 holes. The hole diameter is 0·75 mm in each case. Microphone No. 3 has a back plate with four slots of 2 mm width each. The frequency response of the three different microphones is shown in figure 5 for electrets with a common polarization voltage and all other experimental parameters also kept identical. It is found that microphone No. 1 is more sensitive at frequencies above 1500 Hz and below 300 Hz whereas microphone No. 2 has a larger sensitivity in the frequency range 300 Hz to 1500 Hz. Microphone No. 3 is the most insensitive throughout the frequency range studied.

Since the restoring force on the electret foil is provided by the elastic forces of the air cushion between the foil and the back plate, it has been generally assumed that the microphone back plate must be constructed so as to provide many shallow air cavities for good and constant sensitivity. When no ridges are made in the back plate the restoring force is governed by the stiffness of the foil and the microphone does not have good sensitivity. These conclusions are in agreement with our observations shown in figure 5.

In all measurements referred to above a hole in the body of the microphone connects the air cushion between the back plate and the electret foil to the atmosphere. We have also investigated the effect, on the response of microphone No. 1, of closing this hole. In figure 6 these results are shown and compared with the results when the hole is open. It is found that when this hole is closed the microphone response decreases significantly in the frequency range 100 to 500 Hz while there is a small increase in sensitivity near 1000 Hz. It is felt that these changes are due to some kind of resonance effects.

2.6 *Comparison of a microphone containing a temporarily polarized foil with one containing a permanently polarized foil*

In an earlier paper (Rai *et al* 1981) we have already reported the results of our parametric investigations on a microphone containing a permanently polarized electret

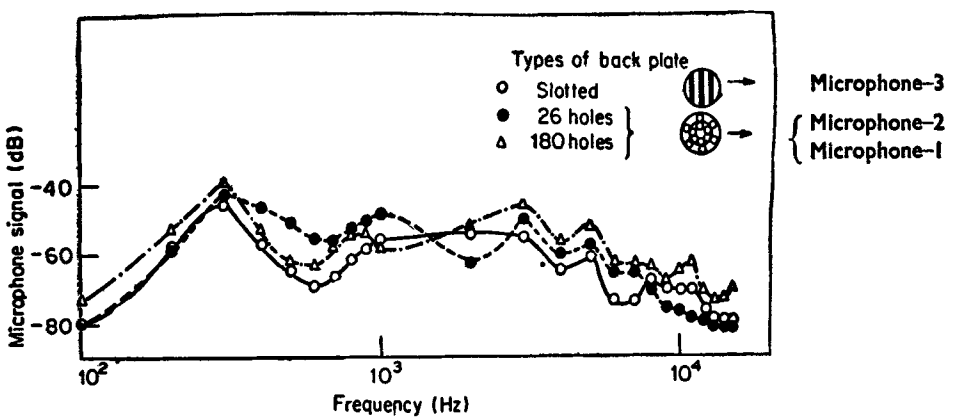


Figure 5. Frequency response of microphone with different types of back plate.

foil. It is found that a foil polarized at 130°C with a DC field of $1{\cdot}5 \times 10^4$ volts/cm gives the most satisfactory results. We have compared the performance of a microphone containing an electret film polarized in this manner with another microphone containing an identical electret film which has been temporarily polarized with a DC field of 10^5 volts/cm. For the sake of comparison the response of a microphone containing a foil permanently polarized at the room temperature was also studied. The result as compared in figure 7 indicate clearly that as far as the overall frequency response is concerned the film permanently polarized at 130°C gives the best results. It is to be noted, however, that for most of the frequency range the temporarily polarized film also gives good sensitivity and is better than the one permanently polarised at room temperature.

3. Spectral measurements

3.1 *Photoacoustic spectrometer*

A single beam photoacoustic spectrometer has been fabricated in our laboratory to study the photoacoustic spectrum of solid and liquid samples. The experimental arrangement is shown in figure 8.

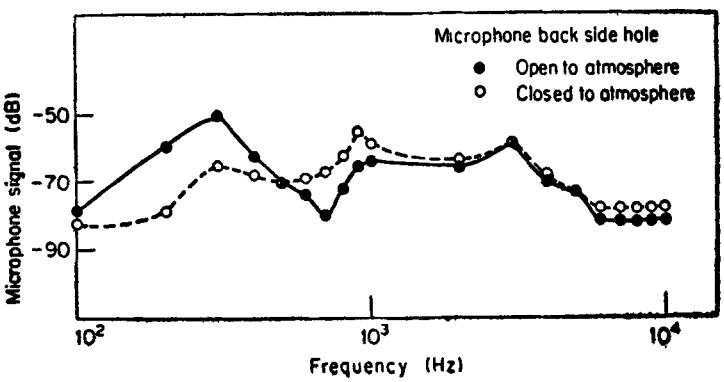


Figure 6. Frequency response of microphone with closed and open hole in the body of microphone.

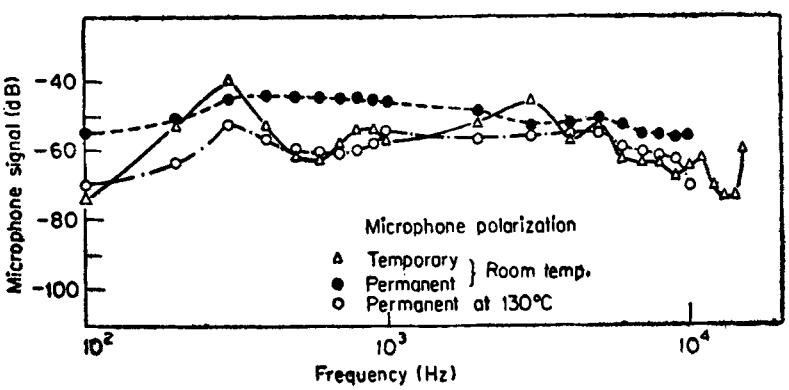


Figure 7. Frequency response of microphone for different polarization technique of diaphragm.

The light source is a Phillips 600W tungsten halogen lamp. The light from the lamp is focussed using two plano-convex lenses on the entrance slit of a (CEL HM 104, 0·25 m grating) monochromator having a band pass of $\simeq$ 8 nm. A variable speed mechanical chopper (EG & G PARC Model 125A) is used for modulation of the incident light beam. We have used a comparatively low chopping frequency of 22.5 Hz (corresponding to 27 Hz for 60 Hz mains) in order to obtain a sufficiently large signal-to-noise ratio.

The construction of the photoacoustic cell is shown in figure 9. The cell was machined from a rectangular block of aluminium. The microphone and the

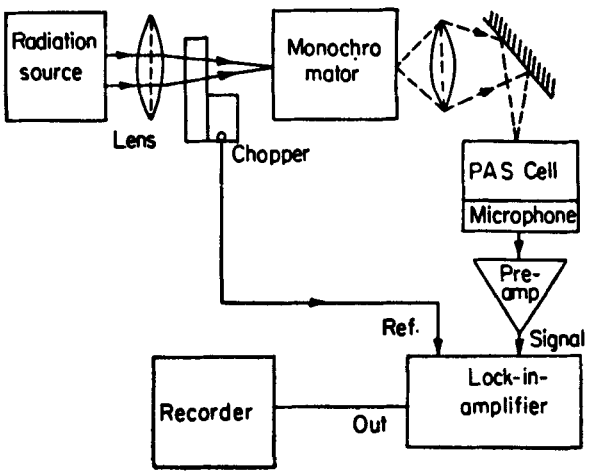


Figure 8. Schematic diagram of the single beam photoacoustic spectrometer.

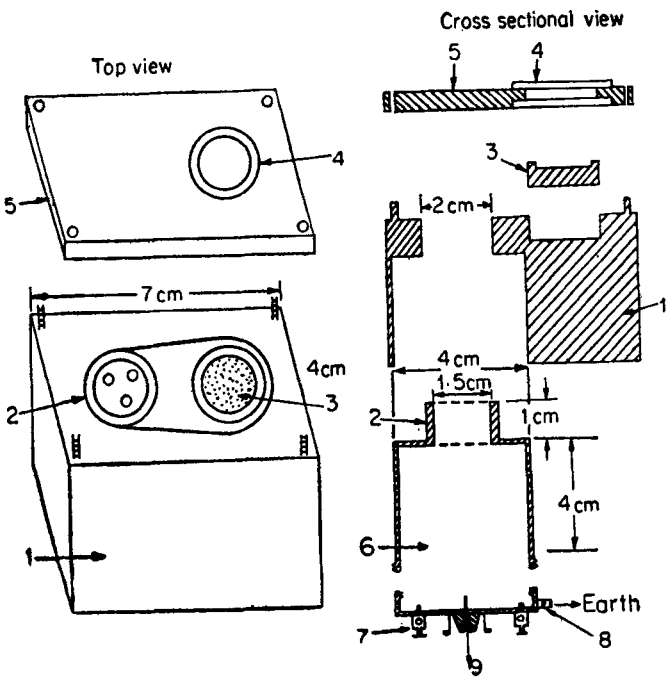


Figure 9. Photoacoustic cell.

associated preamplifier system is inserted into the cell from the lower side while the modulated beam of light enters from the top of the cell. The photoacoustic cell was so designed that the enclosed volume is air tight and is comparatively small. A window of large area (compared to the sample area) is used in order to minimise the effect of scattered light. We have used a Sennheiser microphone capsule (KE II-433) with a preamplifier and biasing system as shown in figure 10. Electret microphones fabricated in our laboratory have also been used for some experiments. The microphone and the preamplifier are kept very close to one another so as to minimise the pick-up noise. We use sample cups made of steel and with outside dimensions such that they fit snugly in the space made for them in the aluminium block. The light coming out of the exit slit of the monochromator is focussed onto the sample with a plane mirror and a convex lens (figure 8). The output signal from the photoacoustic cell goes into the signal channel of a (EMCO Model EE 201) lock-in-amplifier while the reference channel uses a signal from the chopper. The photoacoustic spectrum was normalized using the signal obtained when carbon black was used in place of the sample.

The performance of the photoacoustic spectrometer was tested by studying the spectrum of carbon (lamp) black. The spectrum is shown in figure 11 and is in very

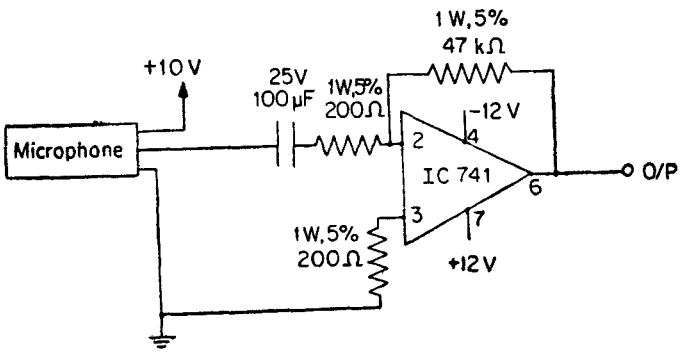


Figure 10. Microphone biasing and preamplifier circuit.

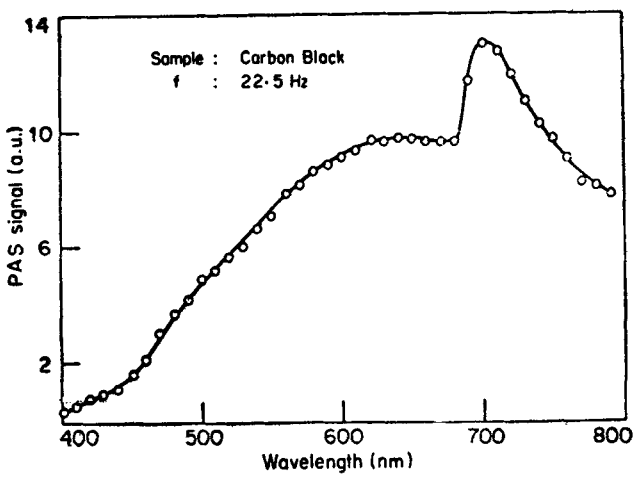


Figure 11. Photoacoustic spectrum of carbon black (lamp).

good agreement with the spectrum as reported by other workers (Ganguly and Rao 1981). The normalization of the sample signal at each wave length is necessary since the spectral output of the lamp is not linear and such normalized spectra are shown and discussed in the following.

3.2 *Comparison of microphones*

The microphone constructed in the manner described in this paper (as well as in Rai *et al* 1981) has been used in the single beam photoacoustic spectrometer and their spectral performance has been compared with a commercial microphone (Sennheiser West Germany, Model KE II-433). The photoacoustic spectra of Nd_2O_3 and PbI_2 powder as recorded by the two microphones using the identical photoacoustic cell are shown in figures 12 and 13.

It is found that the performance of our microphone is quite similar to that of the commercial microphone. The photoacoustic spectrum of Nd_2O_3 recorded by us is seen to be very close to the optical (diffuse reflectance) spectrum (White 1967) and to the photoacoustic spectrum reported earlier (Ganguly and Rao 1981). The PbI_2 photoacoustic spectrum shows an absorption edge at 500 nm. A comparison of sensitivity of the two microphones reveals that our microphone has a sensitivity of $\simeq 1.0$ mV/μ bar whereas for the commercial microphone this value is $\simeq 2$ mV/μ bar. Similar sensitivity has been reported for electret microphone (laboratory made) by other previous workers (Sessler and West 1964, 1966).

3.3 PAS *of rare earth oxides*

We have recorded (figures 14 to 20) the photoacoustic spectra of oxides of several rare earth elements *e.g.* holmium, erbium, neodymium, samarium, dysprosium, gadolinium, praseodymium and terbium. The photoacoustic spectra for all the oxides except

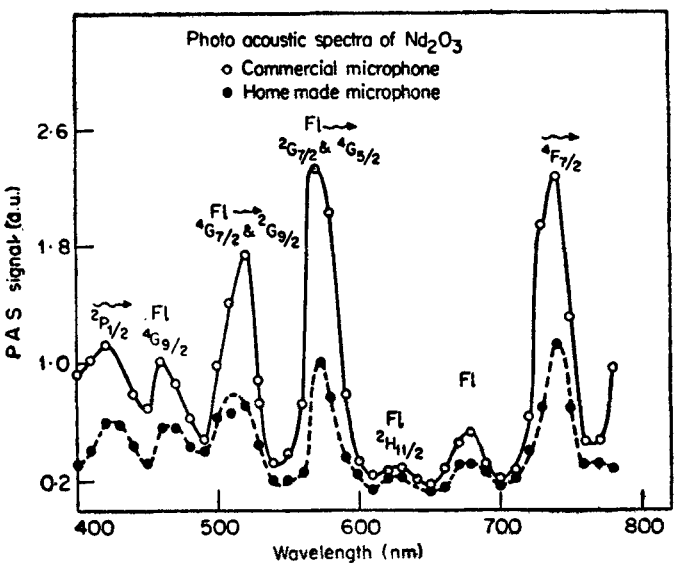


Figure 12. Photoacoustic spectrum of Nd_2O_3 powder.

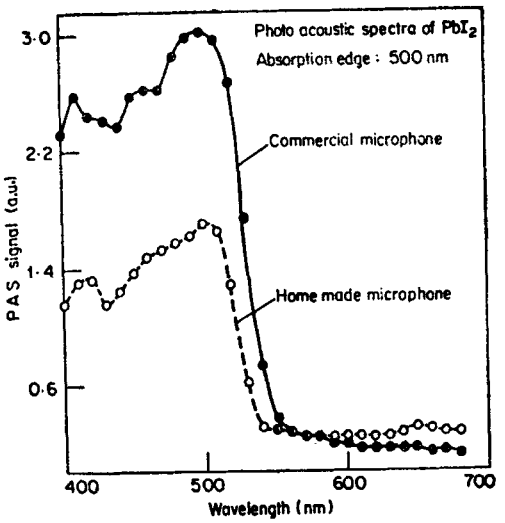
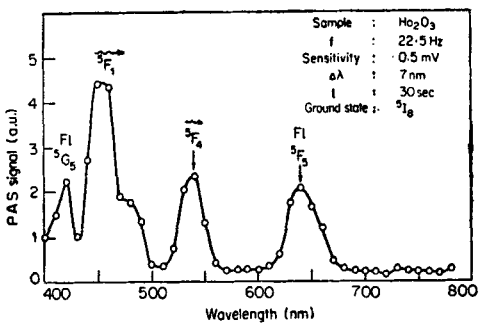
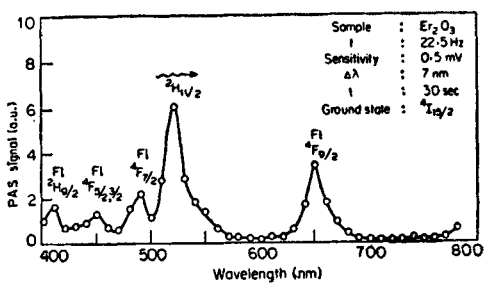


Figure 13. Photoacoustic spectrum of PbI_2 powder (semiconductor).





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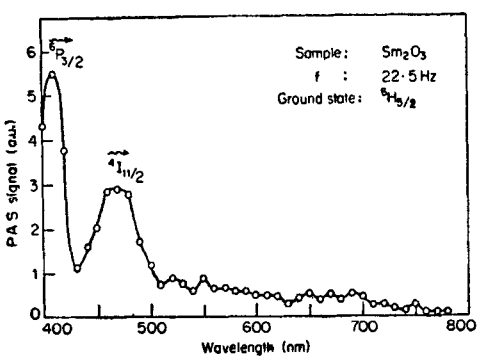

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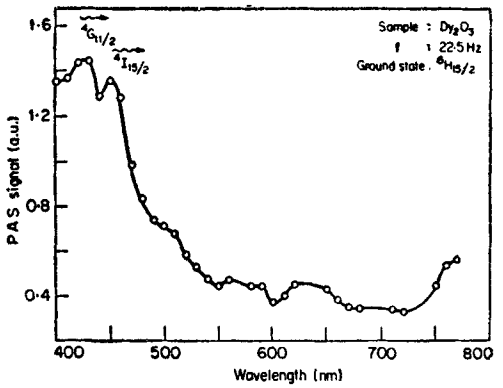

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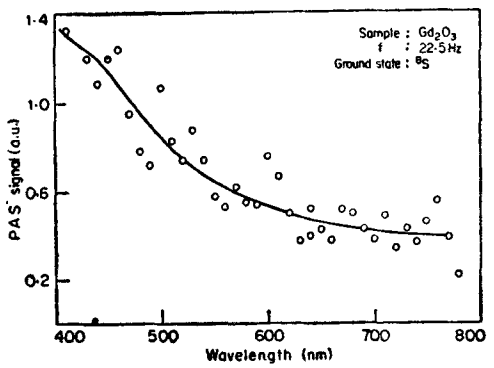

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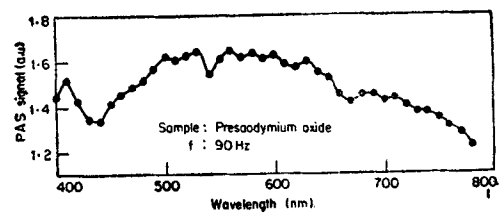

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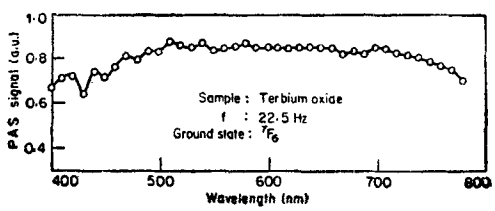

(20)

Figures 14–20. Photoacoustic spectrum of **14.** Ho_2O_3. **15.** Er_2O_3. **16.** Sm_2O_3. **17.** Dy_2O_3. **18.** Gd_2O_3. **19.** Praseodymium oxide. **20.** Terbium oxide.

those of praseodymium and terbium show peaks corresponding to the energy levels of the trivalent metal ions. The levels are easily identified from a comparison with the diffuse reflectance spectra of these oxides reported earlier (White 1967). The (white) Gd_2O_3 powder scatters light very strongly and does not show any peak in the photoacoustic spectrum. This is in agreement with the fact that no optical absorption in the visible region is known. No photoacoustic signal peaks are seen in the

spectrum of praseodymium and terbium oxides. The photoacoustic spectrum of these oxides in fact, differs greatly from the reported diffuse reflectance spectra. It has been suggested (Warenkessel *et al* 1969) that these oxide powders contain a mixture of oxides with different stoichiometric forms. X-ray spectroscopy (Deshmukh *et al* 1981, Warenkessel *et al* 1969) has shown that Pr-oxide powders also contain an intermediate phase between Pr_2O_3 and PrO_2. Even in relatively pure Pr_2O_3 powders it has been conjectured that both Pr^{3+} and Pr^{4+} ions are present in a proportion determined by the stoichiometric concentration of the sample. White in his studies of diffuse reflectance spectra of these compounds had converted the oxides into almost pure Pr_2O_3 (and Tb_2O_3) by heating the sample in an atmosphere of hydrogen for 24 hr at 1200°C before the diffuse reflectance spectra were recorded. Even after this treatment the sample retained some $Pr^{4+}(Tb^{4+})$ ions and characteristic charge transfer transitions were observed in the spectrum.

An important feature of the observed photoacoustic spectra of Ho_2O_3, Er_2O_3, Nd_2O_3, Sm_2O_3 and Dy_2O_3 is that the ionic levels which do not appear in the fluorescence spectrum show up with large intensity. This is in agreement with expectations. Since the photoacoustic signals arise from the heat generated in the sample when excited levels lose their energy by the non-radiative mechanism, the levels which show fluorescence contribute much less to the acoustic signal. The assignment of the photoacoustic spectrum of Ho_2O_3, Er_2O_3, Sm_2O_3, Nd_2O_3 and Dy_2O_3 is done using the energy level diagram for M^{3+}(Dieke 1963) and is shown in the figures.

4. Conclusions

The observations presented in this paper can be summarized as follows:

(a) Electret microphones prepared by using electret foils polarized in the manner described are quite sensitive and suitable for work in photoacoustic spectrometers.

(b) A back plate having several ridges and small holes in contact with the atmosphere is conducive to better sensitivity as is the use of thin electret films.

(c) The variation of microphone sensitivity with time is well described by the available theory.

(d) The photoacoustic spectrometer described here in can be used with confidence to study the PAS of solid samples.

(e) The non-fluorescent levels of the triply ionized rare earth atoms are easily detected in their PA spectrum.

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References

Adams M J, King A A and Kirkbright G F 1976 *Analyst* **101** 73
Colles M J, Geddes N R and Mehdizadeh E 1979 *Cont. Phys.* **20** 11
Callis J B, Gouterman M and Danielson J D S 1969 *Rev. Sci. Instrum.* **40** 1599
Dieke G H 1978 *Spectra and energy levels of rare earth ions in crystals* New York: Interscience)
Deshmukh P C, Deshmukh P and Mande C 1981 *J. Phys.* **C14** 531
Ganguly P and Rao C N R 1981 *Proc. Indian Acad. Sci.* (*Chem. Sci.*) **90** 3
Gray R C, Fishman V A and Bard A J 1977 *Anal. Chem.* **49** 697
Guazzoni G E 1972 *Appl. Spectrosc.* **26** 60
Haensel R, Rabe P and Sountag B 1970 *Solid State Commun.* **8** 1845
Harshbarger W R and Robin M B 1973 *Acc. Chem. Res.* **6** 329
Kirkbright G F 1978 *Opt. Pura Y. Appl.* **11** 125
Luft K F 1943 *Z. Tech. Phys.* **24** 97
McClelland J F and Kniseley R N 1976 *Appl. Opt.* **15** 2658
Rai V N, Singh J P and Thakur S N 1981 *Res. Ind.* **26** 165
Rosencwaig A 1973 *Opt. Commun.* **1** 305
Rosencwaig A 1978 *Advances in electronics and electron physics* (New York: Academic Press)
Sessler G M and West J E 1964 *Audio Engg. Soc.* **12** 129
Sessler G M and West J E 1966 *J. Acoust. Soc. Am.* **40** 1433
Veingerov M L 1945 *Dokl. Akad. Nauk USSR* **46** 182
Warenkessel J M, Lin S H and Eyring L R 1969 *Inorg. Chem.* **8** 875
White W B 1967 *Appl. Spectrosc.* **21** 167