10
Photoacoustic Spectroscopy and Its Applications in Characterization of Nanomaterials

Kaushal Kumar, Aditya Kumar Singh, and Avinash Chandra Pandey

10.1
Introduction

Photoacoustic (also referred to as optoacoustic) spectroscopy is one among the optical characterization tools and is by far not as popular as other photometry techniques (such as absorption or fluorescence). However, in the literature, it has been described as a gradually progressing method for materials characterization [1]. This technique has great potential to give an insight into the energetic balance of the photothermal and photochemical processes and also into some other aspects such as phase changes and defects in the materials. Nonetheless, the popularity of this technique has been obscured by the extensive mathematical descriptions, high sensitivity to the environment, and lack of suitable high-power tunable excitation sources. Other useless complications have also resulted from the number of different names such as PAC (photoacoustic calorimetry), PAS (photoacoustic spectroscopy), LIOAC (laser-induced optoacoustic calorimetry), LIOAS (laser-induced optoacoustic spectroscopy), PTRPA (pulsed time-resolved photoacoustics), and LPAS (laser photoacoustic spectroscopy) assigned to the same technique, using the same physical principle: the photoacoustic (PA) effect. Inappropriate names or nonstandardized language confuse the readers.

In the term photoacoustic, the prefix photo refers to photons as excitation source and acoustic refers to generation of sound. What, sound? Yes!! There is really a sound. The periodic light excitation of the specimen generates sound waves, and the technique that senses these sound waves is known as photoacoustic spectroscopy. In short, this is a technique of listening to the interaction of radiation with matter. The first attempt in this path was done by Alexander Graham Bell in 1881 [2, 3]. He discovered that when periodically chopped sunlight is focused on a sample in an airtight cell to which a hearing tube was connected, a sound effect was produced. He named this device as photophone. In addition, he noted a similar effect when infrared or ultraviolet light was used.

The heat (and hence rise in temperature) in the samples originates because of the nonradiative processes that occur after photon excitation. Any kind of sample that absorbs energy will liberate at least a part of the excitation energy in this way,
and hence the methods to measure this nonradiative part is applicable to almost all types of samples. The liberated heat energy not only carries the information regarding the absorbed energy but also contains details regarding the thermal properties of the sample. A group of such spectroscopic methods based on the measurement of photoinduced heating of the sample are called the *photothermal methods* [4–9]. Hence, on the basis of photothermal spectroscopy one can measure the liberated heat. The thermalization of a sample or the medium as a result of nonradiative relaxation not only results change in temperature of the sample but also brings about changes in many other parameters such as density, pressure, refractive index, and so on. Hence, there exist a number of photothermal techniques depending on the mode of detection. Only the absorbed light energy contributes to the energy liberated in the form of heat. Scattered or reflected light will not contribute to the photothermal signals. Consequently, photothermal spectroscopy more accurately measures optical absorption in highly scattering solutions, in solids and at interfaces. PAS is one such photothermal technique.

Earlier, Bell’s demonstration was evidently regarded as a curiosity of no functional or scientific value and was quickly forgotten. The discovery of laser in the year 1960 is credited with popularizing this technique, and at present, this technique has become one of the important tools to characterize the materials, especially nanomaterials. This novel technique has no restriction on the sample’s physical state and is equally suitable for the study of biological systems and surfaces of solids. The technique can be applied to investigate absorption spectra, fluorescence yields, depth profiles, phase transitions, thermal conductivities, and many others [9–12]. The characterization of nanomaterials through this technique is very important, and this spectroscopy can visualize the dark part of the nanomaterials. The nanomaterials possess higher electron–phonon coupling that gives rise to large nonradiative relaxations, and hence nanomaterials have become an important tool to identify malignant cells and their treatment in the living body. The PA microscopy of the living body is the hottest topic of research nowadays. The future is for nanomaterial-based devices, so it is very important to study light-to-heat conversion in nanomaterials using the PA technique. This technique is very simple, easy to fabricate in the laboratory with least instrumentation, applicable to materials in any phase (solid, liquid, and gas), and finally has a large impact.

This chapter briefly describes the PA technique and its application in material characterization. The author’s main aim is to familiarize the reader with this technique, its fabrication in the laboratory, and characterization of solid samples.

### 10.1.1 Theory of the Signal Generation

Rosencwaig and Gersho (R–G) modified earlier theories and accounted the universally accepted one for all observed effects in PAS of solids. The detailed discussion of the theory can be found in the original work [13]. Here, the author has given only the main outcome of the theory and the basic formulae useful for the analysis of solid-phase samples.
R–G suggested a simple model based on previous arguments and derived a mathematical expression for the resulting pressure fluctuations. The model is sufficient to describe the PA signal generation in condensed matter. According to the R–G theory, with a gas microphone detection of the PA signal, the signal depends on the generation of an acoustic pressure disturbance at the sample–gas interface. The generation of the surface pressure disturbance, in turn, depends on the periodic temperature at the sample–gas interface. Exact expressions for this temperature are derived in the R–G theoretical model, but the transport of the acoustic disturbance in the gas is treated in an approximate heuristic manner, which is, however, valid in most experimental conditions. The formulation of the R–G model is based on the light absorption and thermal wave propagation in an experimental configuration as shown in Figure 10.1. Here, the sample is considered to be in the form of a disc of thickness $l$. It is assumed that the back surface of the sample is in contact with a backing material of thickness $l_b$ and the front surface is in contact with a gas column of length $l_g$. It is further assumed that both gas and backing material are not light absorbing. The following are the parameters used in the R–G model:

- $k$: the thermal conductivity (cal cm$^{-1}$s$^{-1}$°C$^{-1}$)
- $\rho$: the density (g cm$^{-3}$)
- $C$: the specific heat capacity (cal g$^{-1}$°C$^{-1}$)
- $\alpha = k/\rho C$: thermal diffusivity (cm$^2$ s$^{-1}$)
- $a = \sqrt{\frac{2\pi}{\omega}}$: thermal diffusion coefficient (cm$^{-1}$)
- $\mu = 1/a$: the thermal diffusion length (cm)

where $\omega = 2\pi f$, with $f$ the modulation frequency of the incident light beam.

The intensity $I$ of the incident radiation on the surface is assumed to have the form

$$I = \frac{1}{2} I_0 (1 + \cos \omega t)$$  (10.1)

When this sinusoidally modulated light beam of intensity $I_0$ is incident on a solid sample having an absorption coefficient $\beta$, the heat density generated at any point...
due to the light absorbed can be represented by

$$H = \frac{1}{2} \beta I_0 e^{\beta x} (1 + \cos \omega t)$$  \hspace{1cm} (10.2)

The thermal diffusion equation in the solid (taking into account the distributed heat source) can be written as

$$\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha} \frac{\partial \theta}{\partial t} - \frac{\beta I_0 \eta}{2k} e^{\beta x} (1 + e^{i\omega t}) \quad \text{for} \quad -l \leq x \leq 0 \hspace{1cm} (10.3)$$

For the backing material and the gas, the heat diffusion equations may be written as

$$\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha_b} \frac{\partial \theta}{\partial t} \quad \text{for} \quad -(l_b + l) \leq x \leq -l \hspace{1cm} (10.4)$$

$$\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha_g} \frac{\partial \theta}{\partial t} \quad \text{for} \quad 0 \leq x \leq l_g \hspace{1cm} (10.5)$$

where $\theta$ is the temperature and $\eta$ the light-to-heat conversion efficiency. Here, the subscripts $b$ and $g$ represent the backing and gas, respectively. The real part of the complex-valued solution $\theta(x, t)$ of Eqs. (10.3–10.5) is the solution of physical interest and represents the temperature in the cell relative to ambient temperature as a function of position and time.

After imposing appropriate boundary conditions for the temperature and heat flux continuity and neglecting heat flow through convection in the gas under steady-state conditions, the explicit solution to the complex amplitude of the periodic temperature at the solid–gas boundary can be obtained as

$$\theta_0 = \frac{\beta I_0}{2k (\beta^2 - \sigma^2)} \times \left[ \frac{(\gamma - 1) (b + 1) e^{\sigma l} - (\gamma + 1) (b - 1) e^{-\sigma l} + 2 (b - \gamma) e^{-\beta l}}{(g + 1) (b + 1) e^{\omega l} - (g - 1) (b - 1) e^{-\sigma l}} \right]$$  \hspace{1cm} (10.6)

where

$$b = \frac{k_b a_b}{ka}, \quad g = \frac{k_g a_g}{ka}, \quad r = (1 - i) \frac{\beta}{2a}, \quad \sigma = (1 + i) a$$

Periodic heat flow from the solid to the surrounding gas produces a periodic temperature variation in the gas. The time-dependent component of the temperature in the gas attenuates rapidly to zero with increasing distance from the surface of the solid. At a distance of $2\pi \mu_g$, where $\mu_g$ is the thermal diffusion length of the gas, the periodic temperature variation in the gas is effectively fully damped out. Thus, there is a boundary layer of gas, which is only capable of responding thermally to the periodic temperature on the surface of the sample. This layer of gas expands and contracts periodically and thus can be thought of as acting as an acoustic piston on the rest of the gas column, producing an acoustic pressure signal that travels through the entire gas column. Assuming that the rest of the gas responds adiabatically to the action of the acoustic piston, the adiabatic gas law can be used to
derive an expression for the complex envelope of the sinusoidal pressure variation \( Q \) as

\[
Q = \frac{\gamma P_0 \theta_0}{\sqrt{2T_0 l_g a_g}} \tag{10.7}
\]

with \( \theta_0 \) given by Eq. (10.6). Symbols \( \gamma, P_0, \) and \( T_0 \) are the ratio of heat capacities of air, ambient pressure, and temperature, respectively.

Equation (10.7) can be used to evaluate the magnitude and phase of the acoustic pressure wave produced in the cell due to the PA effect. However, a useful interpretation of the above equation is rather difficult in the present form. Hence, some special cases, according to the experimental conditions, have to be considered to get a clear physical insight. In fact, three lengths related to the sample, namely, the physical length \( l \), thermal diffusion length \( \mu \), and optical absorption length \( l_\beta = (1/\beta) \) can be made use of in arriving at different special cases.

10.1.2 Optically Transparent Solids \((l_\beta > l)\)

- **Case 1(a): Thermally thin solids \((\mu \gg l; \mu > l_\beta)\)** This condition results in

\[
Q = \frac{(1 - i)\beta l}{2a_g} \left( \frac{\mu_b}{k b} \right) Y \tag{10.8}
\]

with

\[
Y = \frac{\gamma P_0 I_0}{2\sqrt{2T_0 l_g}} \tag{10.9}
\]

Here, the acoustic signal is proportional to \( \beta l \) and varies as \( f^{-1} \). Moreover, the signal is now determined by thermal properties of the backing material.

- **Case 1(b): Thermally thin solids \((\mu > l; \mu < l_\beta)\)** This case is different from the earlier one in that while the thermal diffusion length of the sample is larger than the length of the sample it is smaller than the absorption length in the sample. Under approximations, the signal behaves in the same manner as in the previous case.

\[
Q = \frac{(1 - i)\beta l}{2a_g} \left( \frac{\mu_b}{k b} \right) Y \tag{10.10}
\]

- **Case 1(c): Thermally thick solids \((\mu < l; \mu \ll l_\beta)\)**

\[
Q = -i \frac{\beta \mu}{2a_g} \left( \frac{\mu}{k} \right) Y \tag{10.11}
\]

Only light absorbed within the first thermal diffusion length contributes to the signal in spite of the fact that light is being absorbed throughout the length of the sample. The signal varies with frequency as \( f^{-3/2} \).
10.1.3

Optically Opaque Solids ($\beta \ll l$)

In this case, most of the light is absorbed within a very small thickness of the sample near the front surface.

- Case 2(a): Thermally thin solids ($\mu \gg l; \mu \gg l_\beta$)

$$Q = \frac{(1 - i)}{2a_g} \left( \frac{\mu b}{kb} \right) Y$$  \hspace{1cm} (10.12)

This expression shows that the acoustic signal is independent of $\beta$ of the absorption coefficient as the whole radiation energy is absorbed. The frequency dependence is of the type $f^{-1}$.

- Case 2(b): Thermally thick solids ($\mu < l; \mu > l_\beta$)

$$Q = \frac{(1 - i)}{2a_g} \left( \frac{\mu}{k} \right) Y$$  \hspace{1cm} (10.13)

This is analogous to Eq. (10.12), but the sample now depends on the thermal properties of the sample rather than on the backing material as in previous case. Again the signal varies as $f^{-1}$.

- Case 2(c): Thermally thick solids ($\mu \ll l; \mu < l_\beta$)

$$Q = -i \frac{\beta \mu}{2a_g} \left( \frac{\mu}{k} \right) Y$$  \hspace{1cm} (10.14)

It shows that the acoustic signal is proportional to the absorption coefficient and the thermal properties of the sample. It also varies as $f^{-3/2}$. A schematic representation of the different cases is given in Figure 10.2.

---

**Figure 10.2**  Schematic representation of various cases of optically transparent solids and optically opaque solids.
The cases discussed so far can be used in the PA study of any kind of sample. One of the important results of the R–G theory is that the PA signal is always linearly proportional to the incident light intensity, irrespective of the sample properties and cell geometry. In cases 2(a) and 2(b), we have seen that the PA signal is independent of the optical absorption coefficient of the sample. In these cases, therefore, the only term in Eqs. (10.12) and (10.13) that depends on the wavelength of the incident radiation is the light source intensity $I_o$. Thus, it is clear that the PA spectrum of an optically opaque sample ($\mu > l_\beta$) is simply the power spectrum of the light source.

10.1.4 Three-Dimensional Heat Flow Model

The R–G theory gives a simplified one-dimensional heat flow model. Quimby and Yen [14] recently studied the heat flow problem in three dimensions both theoretically and experimentally. They concluded that if the lateral dimensions of the cell are equal to or less than a few times the thermal diffusion length of the gas, the one-dimensional treatment is not satisfactory. A lower limit is obtained for the chopping frequency for a given cell diameter below which the one-dimensional theory is no longer adequate. This minimum frequency is

$$f_{\text{min}} = \frac{1}{2} \frac{\alpha_g}{D^2}$$

where $D$ is the diameter of the sample chamber and $\alpha_g$ is the thermal diffusivity of the gas. Quimby and Yen found that the one-dimensional theory of the PA effect in solid samples is applicable only if the thermal diffusion length of the gas is lesser than the radius of the sample chamber.

10.1.5 Thermal Diffusivity

According to the one-dimensional heat flow model of R–G, the pressure fluctuation in the air inside the chamber is given by

$$P = \frac{\gamma P_0 I_0 (a_g a_s)^{1/2}}{2\pi l_g T_0 k_s f \sin h (l_g \sigma_s)} e^{i(\omega f - \pi/2)}$$

where $\gamma$ is the ratio of specific heat capacities of air, $P_0$ and $T_0$ are the ambient pressure and temperature, $I_0$ is the radiation intensity, $f$ is the modulation frequency, and $l_j$, $k_j$, and $\sigma_j$ are the length, thermal conductivity, and the thermal diffusivity of the medium. $j = g$ refers to the gas, and $j = s$ refers to the solid sample. $\sigma_j = (1 + i)\sigma_j$ where $\sigma_j = (\pi f / \alpha_j)^{1/2}$ is the thermal diffusion coefficient of the medium $j$.

For a thermally thin sample (i.e., $l_g a_s << 1$), under approximation, the above expression implies that the PA signal amplitude for the thermally thin sample varies as $f^{-3/2}$, and the phase is insensitive to the variation in the modulation frequency. For a thermally thick sample, the amplitude of the PA signal decreases...
exponentially with the modulation frequency, while the phase decreases linearly with $b\sqrt{f}$. Hence, thermal diffusivities of sample ($\alpha_s$) can be evaluated either from the amplitude data or from the phase response with respect to the modulation frequency.

10.1.6

**Saturation Effect in PAS**

In PAS, the problem of saturation of the signal tends to obscure the relative intensities of the signals at different wavelengths. If the sample has a high value of the absorption coefficient, the PA spectrum becomes almost independent of $\beta$. According to the theoretical model suggested by R–G, only that part of the heat produced in the sample contributes to the signal, which is generated within a depth $\leq \mu$ ($\mu$ is the thermal diffusion length of the sample) below the surface. The incident light also varies as $1/\beta$ in going inside the sample, and they observed that if the whole incident light energy is absorbed in the first thermal diffusion length ($\mu$) then the PA signal becomes independent of the optical absorption coefficient of $\beta$. This accounts for the saturation. The saturation effect can be removed in either of the following ways:

1) By increasing the effective absorption length in the sample, that is, by increasing $l_\beta = (1/\beta)$.
2) By decreasing $\mu$, the thermal diffusion length in the sample.

Dilution of the sample with nonabsorbing materials such as Al₂O₃, silica gel, and MgO has also been used to decrease the saturation effect. It is found that the saturation is decreased to a larger extent if the sample is ground many times the dilution.

Fuchsman and Silversmith [15] have shown that in the process of grinding, the solid samples get coated on the surface of the diluent particles. In addition, the sample is divided into smaller particles through grinding as revealed by electron microscope studies of the ground sample. The effect of the coating is to reduce the number of absorbing particles in the path of the incoming light, which results in an increase in the effective absorption length $l_\beta = (1/\beta)$. With suitable manipulation of $l_\beta \geq \mu$, the saturation disappears, and the characteristic peaks of the sample are revealed. Fuchsman and Silversmith have used this technique to remove saturation in tetraphenylporphyrin employing Al₂O₃ as diluents.

10.1.7

**Photoacoustic versus Absorption Spectroscopy**

The PAS is equivalent to absorption spectroscopy if all the absorbed energy at each wavelength is lost completely by nonradiative processes. There are many differences, however, both in the two spectra as well as in their detection method.
The absorption spectrum is recorded using photomultiplier tubes whose response is proportional to the photon flux, that is, number of photons per unit area, whereas the PA spectrum is obtained indirectly from a microphone reading. The latter is thus proportional to the power of the incident radiation, that is, it depends not only on the number of photons per unit area but also on the energy of the individual photon. It can be easily verified that a photon at 3000 Å can generate twice as much heat as a photon of 6000 Å. The PAS spectrum of carbon black for a given continuous source has been compared with the spectrum of the same source recorded using a radiometer detector. The two spectra are found completely identical. This clearly demonstrates that the PA spectrum is a power spectrum. Since carbon black is an almost perfect absorber, it is normally used for the production of a reference signal for normalization; when the spectrum obtained by a PA spectrometer is divided by the power spectrum of the source then the actual signal is obtained. The PAS therefore provides much more information than the optical absorption spectrum.

**10.2 Instrumentation**

A common PA spectrometer consists of four parts: a periodic (modulated or pulsed) source of illumination, sample chamber, a means of detecting the acoustic signal, and the data acquisition system. A typical spectrometer is shown in Figure 10.3. Various modifications of this fundamental instrumentation have been used to perform a wide variety of PA experiments. There are two kinds of excitation sources available: continuous and pulsed. The measurement can be taken either in scanning mode (obtaining PAS intensity vs wavelength spectra) or in fixed wavelength mode (obtaining PAS intensity vs modulation frequency graph). The PA spectrometer can work either in modulated continuous wave source excitation mode or pulsed source excitation mode.

![Figure 10.3](image-url)  
*Figure 10.3 A typical spectrometer design.*
10.2.1  
**Modulated Continuous Wave Source Spectrometer**

This spectrometer uses a continuous wave radiation source modulated by an external chopping device that can measure the absorption spectra of the samples over the wavelength region of the source. This type of spectrometer is very easy to fabricate in the laboratory. With some modifications in the sample cell, the spectrometer can also measure the thermal conduction property of the samples. The main parts of the spectrometer are discussed below.

10.2.1.1  **Radiation Sources**

The conventional excitation source for obtaining the PAS intensity versus wavelength spectrum is a lamp and monochromator assembly and is the most popular. To obtain the spectra in the ultraviolet-visible-near-infrared region, one can use either a xenon arc lamp or a tungsten halogen bulb in conjunction with a low $f$ number monochromator. The lamp with monochromator can provide continuous tunability from ultraviolet to infrared. The major limitations of this source are low bandwidth and low output power. But lamp–monochromator assembly is mostly used for obtaining spectra in broad range with low resolution. Since signal-to-noise ratio depends on the amount of light falling on the sample, high-power light sources are highly needed. Also, a low $f$ number monochromator that gives high-power light throughput is desirable. In Table 10.1, some suitable lamps for a spectrometer are given.

Lasers have high spectral resolution and power, but they have limited tunability (and fixed wavelength). A laser requires no monochromator, and if it is operated in pulsed mode, it requires no chopper. The laser beam is highly collimated and is advantageous for many cell configurations. The lasers are available in the continuous wave and pulsed wave mode. In the visible region, dye lasers provide a fairly large wavelength range, and with the aid of frequency doubling crystals the range can be extended to the UV region. For the IR region, the recently developed semiconductor and quantum cascade lasers are suitable. There are a lot of commercially available lasers in the market. Figure 1.20 shows wavelengths of some commercially available lasers. Some suitable lasers (continuous wave and

| Lamp name                              | Wavelength region |
|----------------------------------------|-------------------|
| Tungsten halogen lamp (600 W)          | 400 to >1000      |
| Xenon arc lamp (1 kW)                  | 400–2500          |
| Mercury arc lamp                       | 230–650           |
| Carbon arc (cerium core)               | 350–700           |
| Xenon continuous lamp                  | 150–225           |
Table 10.2 Some suitable lasers for PAS.

| Laser type                  | Operation wavelength(s)                                      | Mode and power                  |
|-----------------------------|-------------------------------------------------------------|---------------------------------|
| Helium–neon laser           | 632.8 nm, 543.5 nm, 593.9 nm, 611.8 nm, 1.1523 µm.          | CW, low power                   |
| Argon laser                 | 454.6 nm, 476.5 nm, 488.0 nm, 514.5 nm, also frequency doubled to provide 244 nm, 257 nm | CW with line tunable, high power up to 10 W |
| Nitrogen laser              | 337.1 nm                                                    | Pulsed                          |
| Carbon dioxide laser        | 10.6 µm(9.4 µm)                                             | Line tunable                     |
| Carbon monoxide laser       | 2.6–4 µm, 4.8–8.3 µm                                         | –                               |
| Dye lasers                  | 390–435 nm (stilbene), 460–515 nm (coumarin 102), 570–640 nm (rhodamine 6G), many others including harmonic generation | CW, pulsed and high power tunable |
| Titanium sapphire laser     | 600–1100 nm                                                 | CW, pulsed and high power tunable |
| Nd:YAG laser                | 1064, 532, 355, and 266 nm                                  | CW, pulsed and high power line tunable |
| Optical parametric oscillator (OPO) | 300–3000 nm                                             | CW, pulsed and high power tunable |

Pulsed) for PAS are given in Table 10.2. Detailed information on the lasers is given in Chapter 1 and in Refs. [16–18].

10.2.1.2 Sample Cell

In any PA spectrometer, the PA cell is one of the most important components of the system. The design of the sample cell is very important and depending on whether one is using a single beam system or a double beam system contains two cells. The PA cell design must meet some requirements [5] according to the theoretical studies made by R–G [19]. These requirements have been met with care during the fabrication of the cell. A PA cell should obey the following criteria:

1) The materials of the cell should exhibit good thermal property and be of sufficient thickness to form a good acoustic barrier. Acoustic isolation from the environment can be done by placing the cell in a sound-proof box mounted on springs for isolation from outside vibrations. The table on which the spectrometer is kept could also be isolated.
2) The window above the sample should be transparent in the region of interest and also be of sufficient thickness. The fused quartz window is ideal for this purpose.

3) The light scattered from the sample should not be allowed to fall on the cell walls and microphone diaphragm. For this purpose, the geometry of the cell should be such that the microphone is kept away from the beam path and the sample is directly below the window, with the window being larger than the sample dimensions so that the scattered light or unabsorbed light is reflected out of the cell. Impurities in the sample holder or in the cell that absorb light should be thoroughly eliminated. The cell walls should, therefore, be highly polished, and the sample holder should be easy to clean or replace. It should also be easy to clean the window of the cell periodically.

4) The cell dimensions should be such as to minimize its volume since the PAS signal varies inversely with the cell volume.

5) Thermoviscous damping is an important parameter [20]. The thermoviscous damping coefficient varies as $f^{1/2}$ and becomes important at high frequencies. The cell should, therefore, have a minimum distance between the sample and the window and maximum passageway dimensions between the sample region and the microphone. The dimensions suggested by Rosencwaig are typically 1–3 mm.

6) In order to improve the acoustic signal, it is possible to work with Helmholtz resonance cells or with specially designed cylindrical microphones. Limitations in these cases are the frequency response of the microphone is not flat and the cell cannot be used at frequencies other than the resonance frequency. Typical cell designs are shown in Figure 10.4. The International School of Photonics (ISP), Kochi, India [21] has also developed some PA cells keeping in mind the optimum signal-to-noise ratio.

In general, the microphone section is connected through a narrow passage with sample section. The resonance effects between volumes connected by a narrow passage should be avoided. In case of resonance condition, the signal versus frequency response may not meet the theoretical requirements as discussed earlier for the one-dimensional model. The usual cell geometry is such that the flat electret microphone is mounted perpendicular to the direction of incidence of light (Figure 10.4). In the one-dimensional model, the thermal waves in the gas phase propagate in the direction directly opposite to that of the incident light. The closest approximation to such a cell design is given by Aamodt et al. [22]. These authors have shown that the signal strength is maximum when $\mu = l$, the length of the gas phase. Ferrell and Haven [23] have used a configuration in which the microphone is placed opposite the incident light direction (Figure 10.4c). The sample is placed on a paper positioned between the window and the microphone. A pinhole in the paper is sufficient to connect the microphone and sample compartments to obtain signals without distortion or diminution.
10.2 Instrumentation

Coupling gas
Light beam
Optical windows
Microphone
Metal cell
Sample holder
Sample

(a)

Figure 10.4 Examples of indirect PA cells: (a) indirect cell configuration (Rosencwaig [20]), (b) separate microphone and sample chamber (Helmholtz), and (c) cell design from Ferrell and Haven.

10.2.1.3 Modulation Techniques

Light beam modulation is required in order to observe a PA signal. Several modulation methods that fall under either amplitude modulation or frequency modulation are used. The amplitude modulation is the most commonly used technique.

The use of a mechanical chopper is an inexpensive and efficient way of amplitude modulation. The high-precision, variable-speed and low-vibration noise choppers are available commercially. The depth of modulation of mechanical choppers is 100%. It can also be easily fabricated in the laboratory.

The electro-optic method is also used and is superior to the mechanical method. It involves changing the plane of polarization of the incoming polarized laser beam in a nonlinear crystal ammonium dihydorgen phosphate (ADP), potassium dihydorgen phosphate (KDP) with the application of a modulated electrical field.
to the crystal. The beam can be modulated in square, triangular, sinusoidal, or any other form by this method. The modulation range is 0–20 MHz, and depth is as high as 100%. The electro-optic modulators are expansive and wavelength specific. Acousto-optic modulators are also in use. When high spectral resolution is required with tunable laser sources, frequency modulation is preferred. Amplitude modulation has the disadvantage of window absorption that can be eliminated by using this technique. Other details can be found in Refs. [5, 6, 9].

10.2.1.4 Signal Detectors
There are several methods available for detecting the acoustic signal. These can be broadly classified into three groups: pressure sensors, piezoelectric sensors, and temperature sensors. The most utilized method in PAS is pressure sensors, and the most common device is the microphone.

Microphones are available in two types: condenser microphone and electret microphone. The condenser microphone needs a bias voltage to operate, but the electret does not require it, and hence simplify the apparatus. Many commercial bands are available with the choice of sensitivity, bandwidth, size, and noise. Sensitivity as high as $\sim 100 \text{ mV Pa}^{-1}$ is available (e.g., Bruel and Kjaer, Knowles). These microphones are more sensitive than the condenser microphones. The details of the working of the microphone are available in the literature [5, 9].

For detecting the direct PA signal, microphones are typically not suitable because of large acoustic impedance mismatch at the sample–gas interface. Owing to this impedance mismatch, only a small part of the acoustic energy is transferred from sample to coupling gas. To overcome this deficiency, piezoelectric transducers, which are commercially available, are utilized. Examples of such devices are lead zirconate titanate (PZT), lithium niobate, lead metaniobate, quartz, and so on. The sensitivity of piezoelectric PZT transducers is $\sim 3 \text{ V Pa}^{-1}$, which is much smaller than that of the microphone. However, PZT transducers are preferred over microphones in pulsed excitation because of their faster rise times and better acoustic impedance matching. The procedure of mounting piezoelectric devices is described in Ref. [24].

10.2.1.5 Design of the Low-Cost Continuous Wave PA Spectrophotometer
In this section, a simple design of the low-cost PA spectrophotometer is described, which can easily be fabricated in the laboratory. This spectrometer is able to record wavelength-dependent spectra as well as frequency-dependent PA signal with only some modifications in the sample chamber. The following accessories are needed for it:

1) Halogen bulb (1000 W) and diode laser ($\sim 50 \text{ mW}$)
2) A combination of two short focal length plano-convex lenses
3) Optical chopper
4) Low F-number (focal ratio) monochromator
5) Plano-concave mirror
6) Lock-in amplifier
7) Aluminum block, quartz window, condenser microphone, resistances, capacitances, and so on, for sample cell and amplifier section.
8) Recording system.

10.2.1.5.1 Fabrication of Conventional Photoacoustic Cell for Wavelength versus PA Intensity Spectra

On the basis of theoretical explanation of signal generation in a PA cell, which houses the sample chamber and the microphone chamber, the cell must have certain characteristics for optimum use. The design of the cell involves a complex optimization procedure in order to achieve the necessary high signal-to-noise ratio in PA studies. Since the signal amplitude in the PA cell used for solid samples varies inversely with the gas volume, one should attempt to minimize the gas volume. Furthermore, the distance between the sample and the cell window should always be greater than the thermal diffusion length of the gas, since it is the boundary layer of the gas that acts as an acoustic piston generation of the PA signal in the cell. The requirements that give good signal-to-noise ratio are summarized below.

1) The material of the body of the cell should be chosen with good acoustic seal and with walls of sufficient thickness to form a good acoustic barrier. Hence, aluminum metal has been used as the building material.
2) The cell must also be acoustically isolated from any external signal source (e.g., from chopper, room vibrations, etc.).
3) Stray light absorbed at the cell walls results in temperature rise of the cell walls. This results in the generation of large spurious signals that increase noise in the cell.
4) According to Patel and Tam [25], the increases in the temperature of walls ($\Delta T_{\text{WALL}}$), due to the absorption of stray light is given as

$$\Delta T_{\text{WALL}} = \frac{\text{Const}}{\alpha^{1/2} \rho C}$$

where $\alpha$ is the thermal diffusivity of the material, $\rho$ the density of the material, and $C$ the specific heat of the material.
5) The constant contains surface optical absorption and reflection factors. Hence, constriction materials for the PA cell should have small surface optical absorption, large thermal diffusion length, high density, and high specific heat.
6) The window should be optically transparent throughout the wavelength region of interest and should also be a good attenuator of sound; hence, quartz window has been used.
7) Absorption of scattered light by the cell walls and the microphone diaphragm should be minimum; hence, the microphone is positioned away from the beam path and the internal walls of the cell are polished to avoid absorption. The area of the window is large in comparison to the sample area so that any unabsorbed light or scattered light is reflected out of the cell.
8) Since the signal in the PA cell varies inversely with the gas volume in the cell, the gas volume should be minimized. Thus, the air volume contained in the cell is kept small so as to get a large PA signal.

Keeping these requirements in mind, the PA cell may be constructed as per the method described below. To fabricate a sample chamber, take an aluminum block of 10 cm length, 6 cm breadth, and 4 cm height. Drill holes at four corners of the block to tighten the screw and then cut the block into two parts 3:1 ratio in height. The larger part contains the sample chamber and microphone housing. Drill a cylindrical cavity in this block, which will hold a stainless steel sample holder with 1 cm height and 2.0 cm diameter. Construct a sample holder of depth 2.0 mm, which fits into the sample cavity. Make another hole up to the end and about 1.5 cm away from the center of the first hole having the diameter equal to the microphone. Fit the wire-connected microphone in the hole. The surfaces of the microphone and plane of block must be in the same level. Fix the microphone with glue and make sure it is airtight toward the back. The acoustic signal through the wires from the microphone is taken out from the end of the microphone housing to be fed into the input of the preamplifier section. The smaller aluminum plate contains a quartz window of diameter somewhat larger than 2.0 cm and must be just above the sample holder. The window will allow light to fall on the sample. A rectangular channel of 2 mm depth and 1 mm wide is cut into the rubber gasket extending across the sample chamber and reaching to the middle of the microphone chamber. The microphone chamber is about 1 mm deep and is formed in the region between the electret diaphragm and the bottom of the rubber gasket. The above rectangular channel permits air to pass from the sample chamber into the microphone chamber and has a 2 mm² cross-sectional area and is about 25 mm long. The minimum separation between the window and the sample surface is kept to 2 mm to remove any thermoviscous damping of the acoustic signal. Keep the volume of the air column connecting sample chamber to the microphone less than 1.0 cm³ for maximum signal intensity (R–G theory). The whole assembly is tightened into one compact unit with nuts and bolts to form the complete PA cell. Figure 10.5 shows views of a PAS cell.

10.2.1.5.2 Open Photoacoustic Cell Configuration

Open photoacoustic cell (OPC) configuration is a modified and more convenient form of the conventional PA configuration discussed above. In OPC, usually, the solid sample will be mounted directly on top of the microphone, leaving a small volume of air in between the sample and the microphone. It is an open cell detection configuration in the sense that the sample is placed on top of the detection system itself, as in the case of piezoelectric and pyroelectric detection. Consequently, this configuration is a minimum volume PA detection scheme, and hence the signal strength will be much greater than the conventional PA configurations. The major advantage of this configuration is that samples having large area can be studied, whereas in conventional PA cells sample size should be small enough to be contained inside the PA cavity. A schematic representation of a typical OPC is shown in Figure 10.6.
10.2 Instrumentation

Figure 10.5  Design of a simple PA cell. (a) Cross-sectional view of the cell. (b) Vertical view of the cell.

Figure 10.6  A general schematic representation of an open photoacoustic cell. Here, S is the sample, O the o-ring, M the microphone, and C the cell body. R–G theory can be used to derive an expression for the periodic pressure variation inside the air chamber.

10.2.1.5.3 For Frequency versus PA Intensity Spectra
The above-discussed OPC can be used to determine thermal diffusivity of solids. The heat transmission mechanism in OPC is depicted in Figure 10.7. For an optically opaque sample, the entire light is absorbed by the sample at $x = 0$, and the periodic heat is generated at the sample surface. The thermal waves generated

Figure 10.7  Schematic representation of an open photoacoustic cell configuration.
at $x = 0$ will penetrate through the sample to its rear surface. The heat thus reaching the sample air interface at $x = -l_s$ will get attenuated after traveling a small distance called the first thermal diffusion length ($\mu$) in the air. The thermal diffusion length is given by $\mu = \sqrt{2\alpha/\omega}$, where $\alpha$ is thermal diffusivity of air and $\omega$ the modulation frequency of the incident light. Consequently, this periodic heating process arising as a result of the periodic absorption of light at the interface at $x = 0$ results in an acoustic piston effect in the air column in between the sample and the microphone. Pressure fluctuation in air inside the cell for a thermally thin sample can be written in terms of Eq. (10.16), which implies that the amplitude of PA signal from a thermally thin sample varies as $f^{-3/2}$. When the sample becomes thermally thick at high chopping frequencies, the signal varies as $(1/f) \exp(-bf)$, where $b$ is constant. Hence, thermal diffusivity $\alpha$ can be evaluated from signal amplitude data with respect to modulation frequency, provided that the sample becomes thermally thick from thermally thin in the frequency region of interest.

For the measurement of frequency-dependent characteristics of materials, a different configuration is selected. The main aluminum block has size $5.5 \text{ cm} \times 5.0 \text{ cm} \times 2.5 \text{ cm}$, and the top plate has size $5.5 \text{ cm} \times 5.0 \text{ cm} \times 1.5 \text{ cm}$. Two quartz windows, one in the sample chamber and the other in the top plate, are fitted. In this configuration, the microphone is inserted inside and permits front as well as back illumination of the sample films. The view of this cell is shown in Figure 10.8.

The PA signal obtained by a condenser microphone mounted in the microphone chamber of the PA cell is very weak. Therefore, a large amplification is required before feeding it to the lock-in amplifier. A single-stage preamplifier based on IC 741 can be used for the measurements. The circuit diagram of the single stage preamplifier is shown in Figure 10.9. It is operated by a 9 V DC supply. The output impedance of the condenser microphone is very high ($135 \text{ k}\Omega$); therefore, a voltage follower may be added before the amplifier for impedance matching. Depending on the strength of the PA signal obtained from the microphone, the output of the amplifier can be varied by using a $47 \text{ k}\Omega$ potential divider (preset) to prevent the overloading of the lock-in amplifier. In order to eliminate the external noise,
shielded cables British Naval Connector (BNCs) have been used for carrying the signals from the output of the microphone to the input of the preamplifier and the output of the preamplifier to the input of the lock-in amplifier. The use of extended two-stage amplification with a largely controlled (variable) gain enables one to record the PA spectra of any kind of samples. Usually, overloading of the lock-in amplifier occurs when a two-stage preamplifier is used; therefore great care is necessary to eliminate overloading of the lock-in amplifier.

A simple biasing power supply can be made to provide biasing voltage of $\pm 12 \text{ V}$ for operating the preamplifiers.

10.2.1.5.4 Performance Studies

After designing the complete setup according to the diagram shown in Figure 10.3, the next step is parametric studies of the designed setup to ascertain the effects of source power, chopping frequency, gas coupling volume, and so on. Procedures of the parametric studies for optimization of signal-to-noise ratio can be found in Ref. [26]. In order to obtain the wavelength spectra of the sample, there is a need for a reference sample. The fine carbon black sample is used as a reference. It absorbs all the radiation falling on it and converts it into heat energy, which is sensed by the spectrometer. The spectrum obtained from a carbon black sample closely reproduces the power spectrum of the halogen lamp. In Figure 10.10, the power spectrum of the 650 W tungsten halogen bulb is shown in the 340–850 nm region using the carbon black sample.

10.2.2 Pulsed Photoacoustic Spectroscopy

The apparatus needed to perform pulsed PA studies consists again of a light source, sample cell, microphone, and signal processing unit. The difference between pulsed and continuous wave (CW) mode is in the excitation source. The pulsed
spectrophotometer uses light sources that deliver very high peak power radiation. The high peak power makes it possible to perform a variety of applications that are not possible using continuous sources. Accordingly, some modifications in the cell design and in the detectors and electronics have been made.

The pulsed sources are mostly lasers that deliver high peak powers in the range $10^{-3} – 1$ J per pulse. Such lasers include continuously tunable and fixed frequency or line tunable. The popular wavelength tunable lasers are Nd:YAG and N₂ lasers, pumped dye lasers, Ti:sapphire laser, and OPOs (optical parametric oscillators). The tuning range of OPOs is somewhat larger than that of the dye lasers. The commercial OPOs provide a tunable range over the large region, but these systems are very costly. The fixed frequency or line tunable lasers are Nd:YAG laser, N₂ laser, and CO₂ laser.

The sample cell for pulsed PAS must be of a design different from those used in the CW technique in order to minimize extraneous signals generated by the high energy pulses. In general, nonresonant cell configuration is used for low repetition rate lasers, whereas resonant cells are used for high repetition rate lasers. Dewey and Flint [27] have used resonance cell with an excitation frequency that was subharmonic of the cell’s resonance frequency for high repetition rate lasers. This frequency excites only the cell’s lowest radial mode. More details can be found in Refs. [27, 28].

The other factor that influences pulsed PAS cell design is the ballistic acoustic waves generated by sample adsorption. To avoid this, the sample window should be of the highest optical quality and properly cleaned. Poor windows can lead to two types of background signals: adsorption and scattering. The scattering from window imperfections can cause light to strike on/near microphone. This type of
background signal can be suppressed by the use of transparent material for cell construction.

10.3 Applications of PA Spectroscopy to the Nanomaterials

The PA technique has proved to be a very useful nondestructive characterization technique in the fields of physics, chemistry, and recently in biological specimens. The studies can be divided into three main areas – bulk studies, surface studies, and de-excitation studies. The PA technique provides absorption spectra of solid samples. An unpolished sample surface also poses no problems, and the spectra of strongly scattering samples can be easily measured. It has spectral range from the ultraviolet to far IR based on the availability of excitation sources. For semiconductor materials, their band gaps can easily be calculated directly from the absorption edges in the PA spectra of semiconductors. In recent years, nanomaterials have attracted a lot of attention and several novel materials have been developed for various technological applications. One of the most challenging problems in nanomaterials research is their accurate characterization, which is very important for the efficient use of these technologically promising materials. For example, absolute absorption, quantum efficiency, thermal conductivity, and the elastic constants are important parameters for photonic applications. Although the conventional absorption or emission techniques can provide the absorption coefficient, determining the absolute absorption is not possible due to the presence of scattered light. Therefore, a PA technique that is sensitive and immune to scattered or reflected light is required to determine the absolute absorption in the wavelength region of interest. However, the studies of nanomaterials through this technique are very limited and need more research efforts. The studies can reveal the hidden character of the nanomaterials. Some interesting cases are discussed in the subsequent sections.

10.3.1 Determination of Optical Band Gap

The band gap of any material can be obtained using the PA technique. Xiong et al. [29] studied the PA spectra of nanoclusters of ZrO$_2$ of different sizes and found blueshift in the cut off wavelength of the PA absorption edge as the particle size decreases. The authors also found that the thermal constant of the nanoclusters increases significantly with the decrease in average grain size. Inoue et al. [30] applied the PA spectroscopy to evaluate the nonradiative transition of the Pr$^{3+}$ in ZnO powders with various Pr concentrations and sintering temperatures. They found that PA spectra depend on the inner state of the Pr$^{3+}$ in ZnO matrix, where the Pr can easily segregate to the ZnO grain boundaries and form intergranular-phase-based Pr$_2$O$_3$. Figure 10.11 shows the PA spectra of the sample with different ion concentrations. Peaks A$_1$, A$_2$, and B occur because
of nonradiative transitions from Pr$^{3+}$ ions. Peak A$_1$ shows large concentration dependence, whereas peak B appears only for heavily Pr$^{3+}$ doped system. The authors concluded that peak A$_1$ is related to the presence of Pr$^{3+}$ ions in the ZnO grains, whereas peak B occurs because of the presence of Pr$^{3+}$ at grain boundaries. This study is very informative and can be applied to other rare-earth-doped ZnO samples to identify doping sites of ions.

Zhang [31] studied the PA spectra of BaFBr:Eu$^{2+}$ after glow phosphor was prepared in different environments. The author observed that the PA intensity changes with the change in preparation environment. The study concluded that the sample that gives the least PA signal is the most suitable for fluorescence emission.

The semiconducting nanoparticles are very useful for several applications. Cadmium sulfide (CdS) is one of the direct band gap materials. Kuthirummal [10] studied the PA spectra of bulk and CdS nanowires. Figure 10.12 compares the PA spectra between bulk and nanophases. The band gap of bulk CdS powder occurs at 2.39 ± 0.04 eV, which agrees with the literature value of 2.42 eV. The absorption edge of CdS nanowires is much steeper and occurs at a slightly larger value of 2.49 ± 0.04 eV. These data show that there is no significant contribution from quantum-confinement effects because the average diameter of the nanowires was about 50 nm, which is much larger than the calculated Bohr radius of 2.8 nm. The increased steepness might be attributed to the relatively well-ordered structure and size. El-Brolossy et al. [32] have reported the optical absorption spectra of CdSe quantum dots. They found that by increasing the growing time, the redshift of the PA spectra was clearly observed.

Figure 10.13 shows the PA spectra of 8 and 350 nm La$_{0.8}$Sr$_{0.2}$FeO$_3$ nanoparticles, and 300 nm $\alpha$-Fe$_2$O$_3$ commercial crystals, respectively [33]. In these three samples, the Fe$^{3+}$ cations have a similar coordination environment in the crystal structures. Comparing the three curves, the same shape was observed; except the intensity
10.3 Applications of PA Spectroscopy to the Nanomaterials

Figure 10.12 PA spectra of bulk and nano-CdS. Nano-CdS clearly shows increase in band gaps. (Source: With kind permission from the American Chemical Society.)

Figure 10.13 Comparison of photoacoustic spectra of the nanocrystalline La$_{0.8}$Sr$_{0.2}$FeO$_3$ (solid line), the conventional crystalline La$_{0.8}$Sr$_{0.2}$FeO$_3$ (dashed line), and the commercial crystalline $\alpha$-Fe$_2$O$_3$ (dashed-dotted line) with the average particle size of 8 nm, 0.35 and 0.30 µm, respectively, with the inset of the surface photovoltaic spectroscopy (SPS) of the three samples (the meanings of the lines are the same as that above). (Source: Phys. Rev. B, 75 (2007) 045403, Copyright (2007) of The American Physical Society.)

of the PA signals, the intensity of 8 nm La$_{0.8}$Sr$_{0.2}$FeO$_3$ nanoparticle is higher than that of the other two by five to six times. Since the intensities of the PA signals of 350 nm La$_{0.8}$Sr$_{0.2}$FeO$_3$ nanoparticles and 300 nm $\alpha$-Fe$_2$O$_3$ commercial crystals were nearly equal, the effect of both the La$^{3+}$ and Sr$^{2+}$ cations on electron–phonon interaction responsible for the PA signals in the region below the photoelectric threshold of the nanomaterial should be negligible. The most probable reason for
the intensity difference is that there is a high density of surface localized states associating with the Fe$^{3+}$ cation so far as the nano-La$_{0.8}$Sr$_{0.2}$FeO$_3$ is concerned.

Morais [34] has done PA characterization of various magnetic nanoparticles for magnetic drug delivery systems. He found enhancement in the PA intensity of Band-C due to charge confinement as particle size decrease from 10.7 nm to 3.8 nm (Figure 10.14).

10.3.2 Determination of Absolute Quantum Efficiency

PA spectroscopy can also be easily used to measure the absolute quantum efficiency ($\eta$) of the luminescent nanomaterials. The conventional luminescence tools have proved to be very difficult to measure the efficiency. In a luminescence measurement, the number of quanta absorbed from a beam of monochromatic light has to be compared with the number of quanta emitted in a polychromatic light whose distribution in the space is complicated, and therefore a number of correction factors are involved. Another way is the measurement of fluorescence lifetime; this method again suffers from several experimental difficulties such as separate measurement of the nonradiative contribution to the lifetime of the emitting state [35]. The PA method gives the quantum yield by determining the nonradiative part of the absorbed energy. The measurement of the absolute optical energy absorbed $W_0$ and the absolute heat energy generated $W_{\text{heat}}$ provides the fluorescence quantum yield ($\eta$) for a two-level system as $\eta = (W_0 - W_{\text{heat}})/W_0$.

A key issue in measuring fluorescence quantum yield by the above equation is that absolute heat energy is involved. But the PA signal is proportional only to the modulated heat generated. The best way to avoid this is to perform the

![Figure 10.14](image_url)

**Figure 10.14** PA spectra of the manganese-ferrite-based ionic magnetic fluid samples containing nanoparticles with different average diameters (3.8, 6.6, and 10.7 nm). (Source: With kind permission from Elsevier Science.)
PA measurements twice, first with the desired luminescence quantum yield $\eta_r$ and second with the quantum yield altered in a known way. This provides two equations with two unknowns and so $\eta_r$ can be obtained. The details of mathematical formulation and procedure are given in [35–37]. Rosencwaig and Hildum [35] measured the quantum efficiency of the $^4F_{3/2}$ level of Nd$^{3+}$ in silicate glass using this method. A comparison with the lifetime and luminescence method shows good agreement. Figure 10.15 shows PA and relative fluorescence quantum yield versus Nd$_2$O$_3$ concentration in silicate glasses. A more refined experimental procedure has been proposed by Rodriguez et al. [38]. This method does not require any internal standard.

The quantum yield of any material in any form can be obtained using the PA technique.

10.3.3 Determination of Thermal Diffusivity/Conductivity

PAS is a very powerful technique for measuring thermal diffusivity and hence the thermal conductivity of any material. The thermal conductivity decides the applicability of any material in various applications. The thermal conductivity of the nanomaterials changes very differently and that can be monitored with this technique. As thermal diffusion length is the function of chopping frequency, by varying the chopping frequency of optical radiation and consequently the amplitude of the thermal waves, the transition frequency at which a sample changes from thermally thin to thermally thick regime can be known from the amplitude spectrum of the PA signal. By knowing the transition frequency and the thickness

![Figure 10.15](image-url)

*Figure 10.15* Photoacoustic and relative fluorescence quantum yield versus Nd$_2$O$_3$ concentration in silicate glasses. (Source: Reproduced from A. Rosencwaig, Edward A Hildum, *Phys. Rev. B*, 23 (1981), Copyright (1981) by The American Physical Society.)
of the specimen under investigation, the thermal diffusivity ($\alpha$) can be evaluated using the expression

$$\alpha = f_c l^2,$$

where $f_c$ is the critical frequency and $l$ is the sample thickness.

El-Brolossy et al. [32] obtained the thermal diffusivities of CdSe quantum dots and compared them with bulk CdS. The authors found one order enhancement in thermal conductivity of quantum dot CdSe than bulk CdSe. Figure 10.16 shows the plot of PA amplitude versus the inverse of chopping frequency variation for the CdSe quantum dot sample. A distinct change in slope (shown by arrow) determines the critical frequency where the sample goes thermally thin to thermally thick.

George et al. [39] obtained the thermal diffusivity of $\text{Al}_2\text{O}_3-\text{Ag}$ nanocomposites. Chandra et al. [40] obtained thermal diffusivities of $\text{AgI}-\text{Al}_2\text{O}_3$, \text{AgI}-\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ composite materials and the correlation between the thermal diffusivity and electrical conductivity of the composites.

10.3.4 Photoacoustic Spectroscopy in Biology

Use of nanomaterials in biology or medicine is a very new and vast area of research. In the past decade, a number of new works representing the interest of laser PA in biology were published. The applications of PA methods in biophysics and medicine, say, for diagnosis of carcinoma in body, photothermal treatment, and others seem prospective. Bioconjugated nanocontrast agents together with the PA imaging technique can reliably detect, diagnose, and characterize carcinoma cells. A list of some of the applications of nanomaterials in biology or medicine is given in Ref. [41].

![Figure 10.16](source: With kind permission from Springer.)
The fact that nanoparticles exist in the same size domain as proteins makes them suitable for biological applications. However, size is just one of the many characteristics of nanoparticles that make them applicable in biology. Interaction of light with nanomaterials can induce several phenomena such as photon emission, heat generation, and photodissociation. The significance of PA imaging is that it overcomes the problems faced by conventional imaging techniques such as optical imaging and ultrasonic imaging and yields images of high contrast and high resolution in relatively large volumes of biological tissues [42]. In PA imaging, nonionizing laser pulses are delivered into biological tissues. Some of the delivered energy will be absorbed by the tissues and a part of that is converted into heat, leading to transient thermoelastic expansion, and thus wideband (e.g., MHz) ultrasonic emission may be termed as laser-induced ultrasonics. The generated ultrasonic waves are then detected by ultrasonic transducers to form images. It is known that optical absorption is closely associated with physiological properties, such as hemoglobin concentration and oxygen saturation. As a result, the magnitude of the ultrasonic emission (i.e., PA signal), which is proportional to the local energy deposition, reveals physiologically specific optical absorption contrast.

Gold nanoparticles and carbon nanotubes (CNTs) have gained popularity as nanosized contrast agents in PA imaging, and search for others is going on. The PA spectroscopy is a key technique to characterize nanoparticles that can generate enough heat on photon excitation. Figure 10.17 shows application of CNTs in the enhancement of PA contrast. El-Brolossy et al. [43] prepared gold nanoparticles in various shapes and characterized them through PA spectroscopy. PA spectra of gold nanoparticles having rodlike and spherelike structures are illustrated in Figure 10.18. A strong PA signal is observed in the case of the shepherd shape.

![Image of rat blood vessels](image)

Figure 10.17 PA image of rat blood vessels; acquired (a) before carbon nanotube (CNT) injection and (b) after nanotube injection. Bright parts represent optical absorption, here, from blood vessels.
Photoacoustic Spectroscopy and Its Applications in Characterization of Nanomaterials

10.3.5

Determination of Phase Transition with Temperature

PA spectroscopy can identify temperature-induced phase transitions in nanomaterials. To obtain the phase transitions, a variable temperature cell that can be fabricated according to Figure 10.19 is needed. This cell is of resonant type and contains a separate chamber for the microphone.

References

1. Fork, D.C. and Herbert, S.K. (1993) Photochem. Photobiol., 57, 207.
2. Bell, A.G. (1880) Am. J. Sci., 20, 305.
3. Bell, A.G. (1881) Philos. Mag., 11, 510.
4. Demtroder, W. (2003) Laser Spectroscopy: Principles and Applications, Springer.
5. Pao, Y.H. (ed.) (1977) *Optoacoustic Spectroscopy and Detection*, Academic Press, California.
6. Zharov, V.P. and Letokhov, V.S. (1986) *Laser Optoacoustic Spectroscopy*, Springer-Verlag, Berlin.
7. George, N.A. (1992) Photoacoustic and photothermal detection studies on certain photonic materials. PhD thesis. Cochin University of Science and Technology.
8. Hess, P. (ed.) (1989) *Photoacoustic, Photothermal and Photochemical Processes in Gases*, Springer-Verlag, Berlin.
9. Luscher, E., Korpiun, P., Coufal, H., and Tilgner, R. (1984) *Photoacoustic Effect: Principles and Applications*, Friedrich Vieweg & Sohn, Braunschweig.
10. Kuthirummal, N. (2009) *J. Chem. Educ.*, 86, 1238.
11. Somoano, R.B. (1978) *Angew. Chem., Int. Ed. Engl.*, 17, 238.
12. Petrov, V.V., Gemina, E.A., and Lapin, S.A. (1999) SPIE, 3726, 200.
13. Rosencwaig, A. (1978) *J. Appl. Phys.*, 45, 2905.
14. Quimby, R.S. and Yen, W.M. (1979) *Appl. Phys. Lett.*, 35, 43.
15. Fuchsmen, W.H. and Silversmith, A.J. (1979) *Anal. Chem.*, 51, 589.
16. Namibiar, K.R. (2006) *Lasers: Principles, Types and Applications*, New Age International Publishers, New Delhi.
17. Csele, M. (2004) *Fundamentals of Light Sources and Lasers*, Wiley Interscience Publication, New Jersey.
18. Svelto, O. (2009) *Principles of Lasers*, 5th edn, Springer.
19. Rosencwaig, A. (1980) *Photoacoustics and Photoacoustic Spectroscopy*, John Wiley & Sons, Inc., New York.
20. Rosencwaig, A. (1977) *Rev. Sci. Instrum.*, 48, 1133.
21. George, S.D., Kumar, B. A., Radhakrishnan, P., Nampoori, V.P.N., and Vallabhan, C.P.G. (2004) *Opt. Eng.*, 43, 3114.
22. Aamodt, J.C., Murphy, L.C., and Parker, G.J. (1977) *J. Appl. Phys.*, 48, 927.
23. Ferrell, N.C. and Haven, Y. (1977) *J. Appl. Phys.*, 48, 3984.
24. Tam, A.C. and Patel, C.K.N. (1979) *Appl. Phys. Letts.*, 35, 843.
25. Patel, C.K.N. and Tam, A.C. (1981) *Rev. Mod. Phys.*, 53, 517.
26. Pandhija, S., Rai, N.K., Singh, A.K., Rai, A.K., and Gopal, R. (2006) *Prog. Cryst Growth Charact. Mater.*, 52, 53.
27. Dewey, C.F. and Flint, J.H. (1979) *Technical Digest to the Topical Meeting on Photoacoustic Spectroscopy*, Optical Society of America, Ames, IA.
28. Mandelis, A. and Royce, B.S.H. (1979) *J. Appl. Phys.*, 50, 4330.
29. Xiong, Y., Yu, K.N., and Xiong, C. (1994) *Phys. Rev. B*, 49, 5607.
30. Inoue, Y., Okamoto, M., Kawahara1, T., and Morimoto, J. (2006) *J. Alloys Comp.*, 408–412, 1234.
31. Zhang, Y. (1997) *Chem. Phys.*, 219, 353.
32. El-Brolossy, T.A., Abdallah, S., Abdallah, T., Mohamed, M.B., Negm, S., and Talaat, H. (2008) *Eur. Phys. J. Spec. Top.*, 153, 365.
33. Li, K.Y., Yang, F., Tian, Y.J., Liu, R.P., Wang, W.K., and Wang, H.T. (2007) *Phys. Rev. B*, 75, 045403.
34. Morais, P.C. (2009) *J. Alloys Comp.*, 483, 544.
35. Rosencwaig, A. and Hildum, E.A. (1981) *Phys. Rev.*, B 23, 3301.
36. Murphy, J.C. and Aamodt, L.C. (1977) *J. Appl. Phys.*, 48, 3502.
37. Quimby, R.S. and Yen, W.M. (1978) *Opt. Lett.*, 3, 181.
38. Rodriguez, E., Tocho, J.O., and Cusso, F. (1993) *Phys. Rev.*, B 47, 14049.
39. George, S.D., Anappara, A.A., Warrier, P.R.S., Warrier, K.G.K., Radhakrishnan, P., Nampoori, V.P.N., and Vallabhan, C.P.G. (2008) *Mater. Chem. Phys.*, 111, 38.
40. Chandra, S., Rai, S.B., Singh, P.K., Kumar, K., and Chandra, A. (2006) *J. Phys. D: Appl. Phys.*, 39, 3680.
41. Salata, O.V. (2004) *J. Nanobiotechnol.*, 2.
42. Xua, M. and Wang, L.V. (2006) *Rev. Sci. Instrum.*, 77, 041101 (22).
43. El-Brolossy, T.A., Abdallah, T., Mohamed, M.B., Abdallah, S., Easawi, K., Negm, S., and Talaat, H. (2008) *Eur. Phys. J. Spec. Top.*, 153, 361.