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Three-zone furnace: Apparatus to grow doped crystals from two materials which have wide difference in sublimation temperatures

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It is a difficult process to dope a material using sublimation method when the substances chosen for study have different sublimation temperatures. The two substances used for making the doped crystal are to be maintained at their respective sublimation temperatures before they are allowed to interact at a common temperature gradient zone for the desired crystal growth. Therefore it was decided to construct a furnace which will maintain the two substances in their sublimation temperature simultaneously. The apparatus was constructed to grow metal free phthalocyanine (H_2Pc) doped anthracene crystal as they are expected to be active in the entire region (UV-VIS-IR) of the electromagnetic spectrum, for a possible application as a solar cell material. Phthalocyanine (sublimation at 460°C) doped Anthracene (sublimation at 167°C) crystal was successfully grown using this three-zone furnace and was analysed using XRD, IR, TGA and conductivity studies. In general, the furnace will be especially useful for the combined growth of certain substances which do not have a melting point. © *2003 Kluwer Academic Publishers*

1. Introduction

Crystal growth is an art, by which many elements are grown according to their lattice arrangement. Growing doped crystals is a common practice today where selected atoms or molecules are substituted by a suitable dopant. There are many ways for doping a crystal and new techniques are being developed to grow pure and doped crystals. The doping could be achieved by any of the methods namely solution, melt, sublimation, gel etc. If there is no common solvent between the materials then solution method is not suitable for the combined growth of a doped crystal. If doping has to be done with two materials of different melting temperatures then it is not possible to use the usual melt method too. However sublimation method is an alternative method for growing doped crystal. But it is difficult to dope a material using sublimation technique when the substances have different sublimation temperatures. If the doped growth involves two materials with different sublimation temperatures then the substances are to be maintained at their respective sublimation temperatures before they are allowed to interact for the combined growth. Therefore it has been decided to construct a furnace set up which will maintain the substances in their respective sublimation temperatures simultaneously. It is reported by Sugiyama and his co-workers [1] about a vertical three-zone furnace constructed for the growth of $L^{10}BO(Li^{10}B_3O_5)$ optical crystal.

In some cases if there is a wide range of difference between the melting points of two materials, then it is practically not possible to grow the doped crystal. For example, anthracene has the melting point at 217°C [2–5] and metal free phthalocyanine does not have a particular melting point but decomposes above 550°C [6]. Polyaromatic cyclic hydrocarbons when exposed to sunlight results in structural photomodification [7]. In the literature a porphyrin-anthracene system assembled via complementary nucleic acid base pairing is reported [8]. Hence it was desired to grow metal free phthalocyanine (H_2Pc) doped anthracene crystal, as they are good photoconductors in VIS-IR and UV region of the electromagnetic spectrum respectively. Hence H_2Pc doped anthracene crystal is expected to be active in the entire region UV-VIS-IR, and the compound material could be an alternative for a possible solar radiation absorbing material in the entire range of the solar spectrum. When anthracene is in the molten form at 217°C, H_2Pc will remain as a solid, but for doped growth both substances should be brought together in vapour form. Hence a special furnace with three temperature zones was designed. Two zones are meant for maintaining the sublimation temperatures of anthracene and H_2Pc separately and the third zone for maintaining a temperature gradient, which would enhance the nucleation and growth of the crystal. H_2Pc doped anthracene crystals were grown using this three-zone furnace and structural

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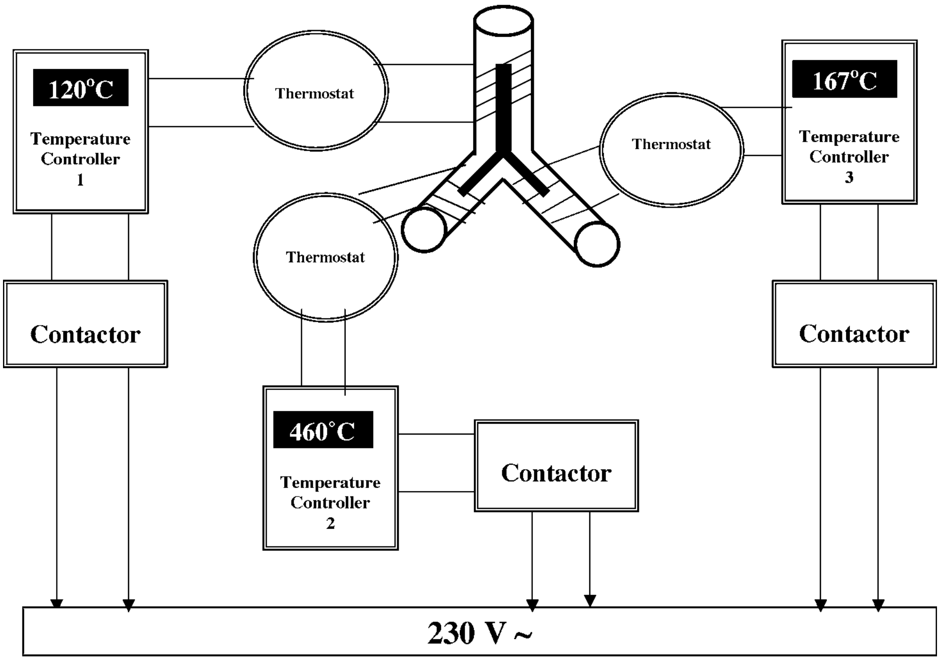

Figure 1 Circuit layout of three-zone furnace.

and spectral studies were done on the crystals. Recently we have reported [9] briefly about the crystal grown using this furnace and in the present paper we are presenting the functioning of the furnace and the characteristics of the crystal grown. For growing crystals of compounds showing a well-defined deviation from stoichiometry, this method of maintaining three temperatures is suggested [10].

2. Furnace setup

The entire arrangement of the furnace set up is shown in Fig. 1. It consists of a 3-leg Pyrex tube (vertical arm of 12.5 cm long and 3.5 cm diameter, side arms of 6.5 cm long and 2.3 cm diameter). Each arm is fitted with a ceramic tube which could be maintained at any desired temperature by use of thermostat and temperature controller system.

3. Experimental procedures

It is desired to grow metal free phthalocyanine (H_2Pc) doped anthracene crystal using this three-zone furnace. Iodine doped Phthalocyanine crystals were earlier grown using a similar experimental arrangement [11, 12]. Anthracene is placed in the left arm of the tube and phthalocyanine in the right arm of the tube. The main stem (vertical) of the tube is connected to a high vacuum pump for a period of 6 hrs and finally evacuated to 10^{-6} Torr. Care was taken not to contaminate the H_2Pc and anthracene powder. At this high vacuum, the side arms of the tube were gently heated to near sublimation temperatures so as to remove the volatile impurities present in the chemical. Finally the glass tube is sealed in vacuum at the top of the tapering end. The sealed tube is placed in the furnace and set for respective sublimation temperatures (Anthracene at 167°C [2], H_2Pc at 460°C [6]). The fluctuation of temperature in this furnace is limited within 1°C by introducing a thermostat between the temperature controller and the furnace. The junctions of side arm with the vertical arm were thermally isolated using glass wool. The main stem of the tube is kept at a temperature gradient of 80°C to 120°C and it is maintained at a lower temperature compared to the temperatures of the side arms and the tapering portion of the tube (about 3 cm) is at room temperature. The portion of the main stem of the tube joining the two arms is kept at 120°C and its tapering end at 80°C. This temperature gradient enhances the nucleation between the sublimates of anthracene and H_2Pc. Three thermocouple-sensing probes made of Chromium-Aluminium monitors the furnace temperature. The entire furnace is covered using ceramic tape and glass wool to avoid loss of heat by radiation [3]. The rates of heating are adjusted in such a way that anthracene and H_2Pc reach the sublimation state simultaneously. The sublimates are led into the temperature gradient region and are allowed to interact to form a doped crystal at a convenient temperature region. The individual temperature profiles of three furnaces are given in Fig. 2. The temperatures of the furnace were maintained for a period ranging from 2 days to one week, which resulted in the increase in thickness of the crystal depending upon the period of heating. At the end of heating, temperatures were slowly reduced to room temperature (over a period of 6 to 8 hours) and the crystals were recovered for further analysis. The crystals obtained were very thin (1 mm) in the form of mostly flakes. The crystals grown were analysed using XRD, IR and TGA.

4. Results and discussion

The concentration of H_2Pc doped onto anthracene is determined as 0.12% by CHN analysis (Heraeus CHN-O-RAPID Analyser). This method could grow the crystals of other concentrations provided the temperature of the furnace is maintained for a longer period ranging to several months. The three-zone furnace was designed to grow phthalocyanine-doped anthracene crystal with the main objective of applying the doped material for a possible solar cell application. Slightly bluish colored crystals in the form of flakes (1mm thick) were formed along the main stem of the tube. The single crystal X-ray reflections from the crystal shows that crystals are highly mosaic. Unit cell dimensions were analysed using Enraf Nonius CAD-4v31 Single Crystal X-ray Diffractometer and the experimental values are compared with the standard values in Table I. H_2Pc

TABLE I Comparison of cell parameters of pure and doped anthracene crystal with standard values

		Experimental values	
Cell parameter	Standard values for anthracene [14, 15]	Anthracene	H_2Pc doped anthracene
a (Å)	8.56	8.51	8.54
b (Å)	6.04	6.01	5.99
c (Å)	11.16	11.21	11.22
α	90°	90°	90°
β	124.7°	124.7°	124.8°
γ	90°	90°	90°
Volume (Å^3)	474.2	471.4	471.3

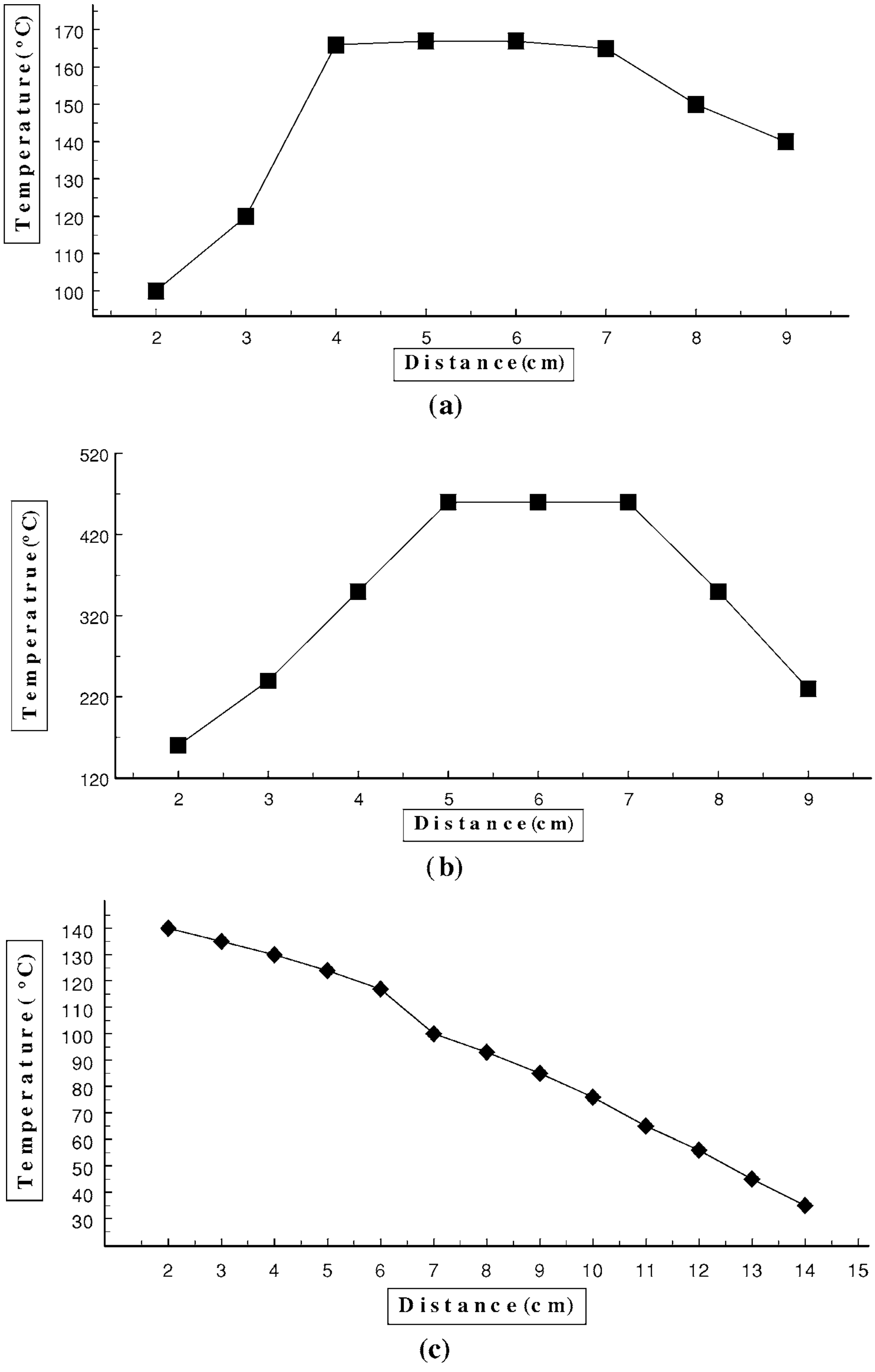

Figure 2 Temperature distribution in the sublimation furnace (a) Anthracene (b) Phthalocyanine and (c) Temperature gradient zone.

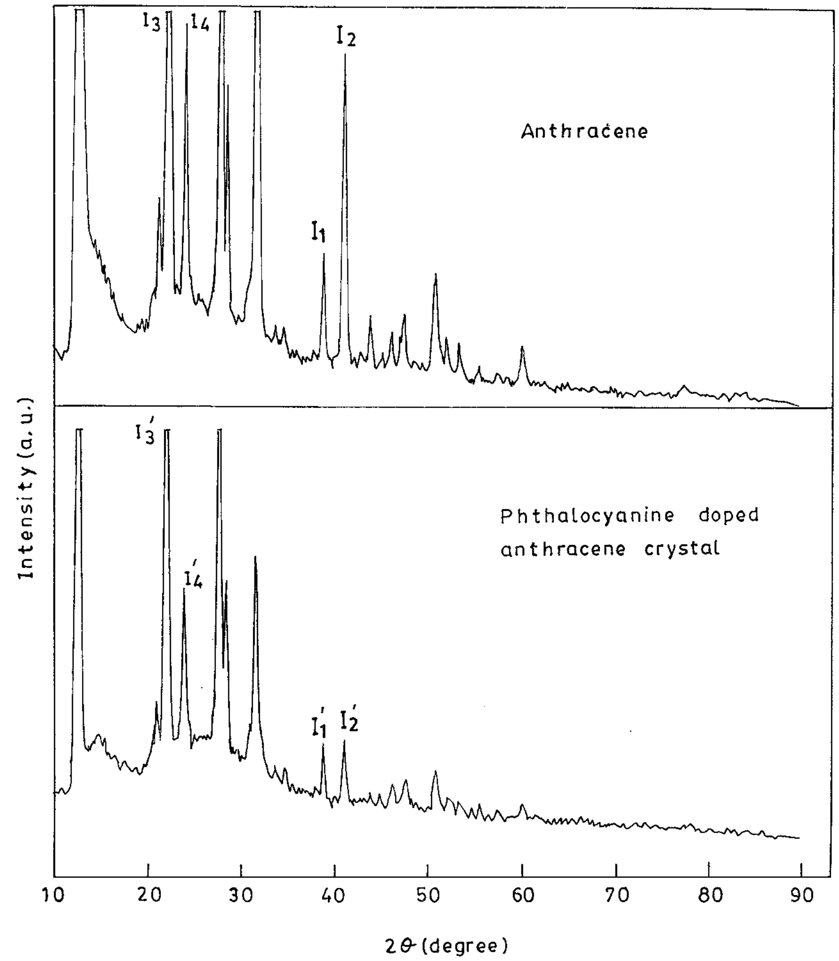

Figure 3 XRD patterns of pure anthracene and H_2Pc doped anthracene crystal.

doesn't make any significant change in the crystal lattice structure of anthracene as it is doped less than 2%. In our earlier paper [13] we have reported H_2Pc doped anthracene co-crystals in which H_2Pc is doped less than 1% without bringing any structural change in anthracene. Also it is reported in the literature [4] that impurities are doped onto anthracene in parts per thousand level. The powder XRD pattern of pure anthracene and H_2Pc doped anthracene crystal is shown in Fig. 3. Even though the position of diffraction peaks for pure and doped anthracene remain the same, the relative intensities of some of the peaks have significantly changed. For example, the corresponding peak intensity ratios (I_1/I_2), (I_3/I_4) of pure anthracene are markedly different from (I'_1/I'_2), (I'_3/I'_4) of H_2Pc doped anthracene crystal.

The IR spectra were taken for H_2Pc and pure anthracene crystal (Fig. 4) using the solvent nujol corresponding to broad peak in the range 2850–3000 cm^{-1}. H_2Pc doped anthracene is recorded in the powder form as it doesn't have a good solvent (Fig. 4). Anthracene spectrum on an average absorbs 50% of the IR radiation, whereas H_2Pc doped anthracene shows almost complete absorption (100%) of the IR radiation. This confirms our expectation that anthracene which is less active in the IR region becomes more active when it is doped with H_2Pc even at low concentration. The IR spectrum of H_2Pc doped anthracene shows a broad peak at 3416.35 cm^{-1} which is assigned as N-H stretch. Also

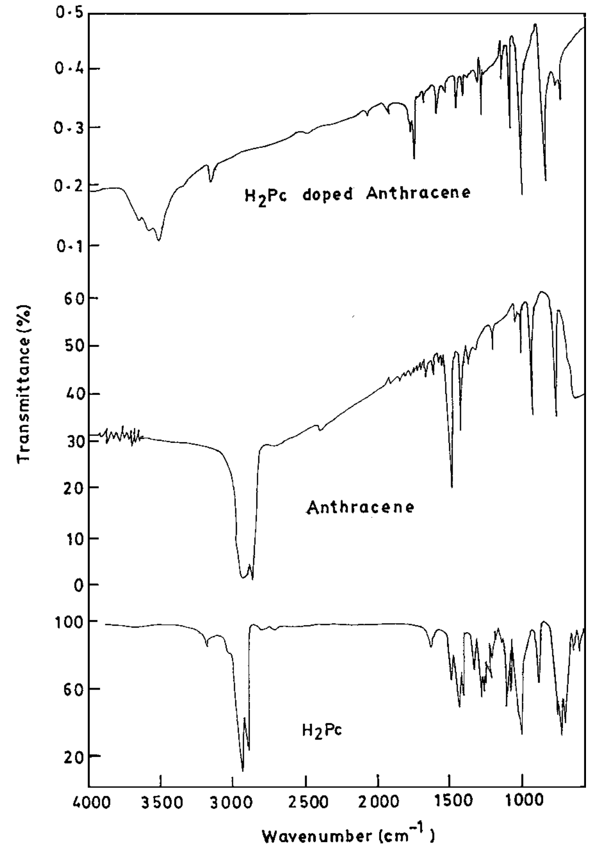

Figure 4 IR spectra of metal free phthalocyanine (H_2Pc), pure anthracene and H_2Pc doped anthracene crystal.

a strong peak at 744.05 cm^{-1} is assigned to N-H deformation. Anthracene being a hydrocarbon doesn't contain nitrogen, whereas H_2Pc contains nitrogen which is incorporated into anthracene due to doping by sublimation and hence it is responsible for producing a broad peak at 3416.35 cm^{-1} and a strong peak at 744.05 cm^{-1}. This clearly shows that H_2Pc is doped onto anthracene by vacuum sublimation using the three-zone furnace. All the other peaks in the IR spectrum are found in both doped and undoped sample which corresponds to standard frequency assignments of anthracene reported in the literature [16]. The spectrum of the H_2Pc doped anthracene crystal is not the linear combination of the spectra of individual materials (Fig. 4) weighted by their respective concentrations. Though the concentration of H_2Pc is 0.12%, IR bands of N-H stretching and deformation modes are dominated in the spectrum of H_2Pc doped anthracene. Intensities of the bands assigned to the guest molecule are much stronger than those due to the host molecule. Such intensity enhancements of some bands occur in charge transfer (CT) complex crystals. When pure anthracene is doped with an

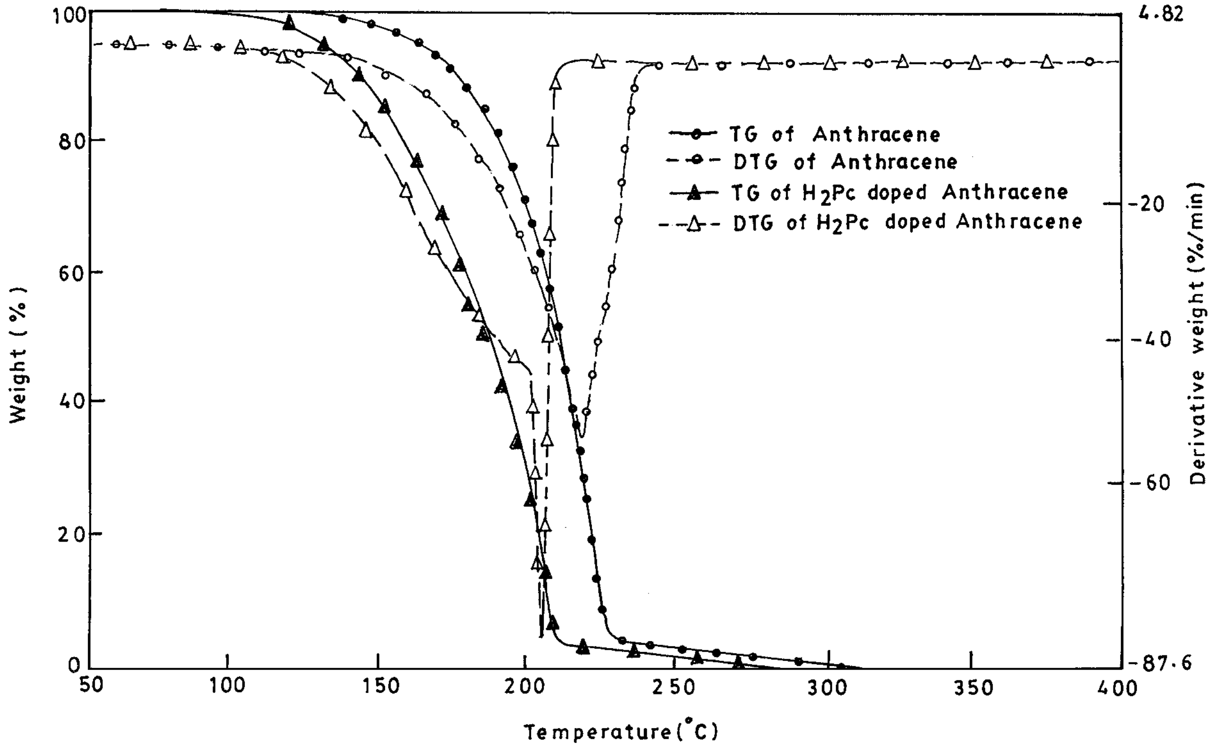

Figure 5 TGA of pure anthracene and H_2Pc doped anthracene crystal.

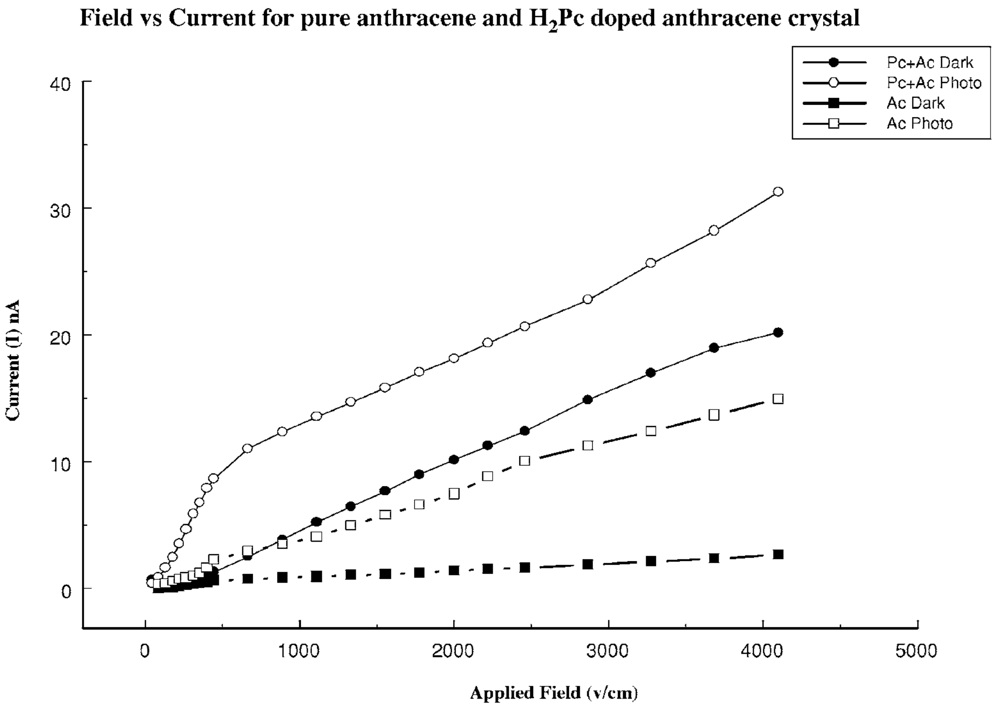
Field vs Current for pure anthracene and H_2Pc doped anthracene crystal

Figure 6 Field vs Dark, Photocurrent for pure and doped anthracene crystal.

objective of increasing its conductivity, it behaves like a charge transfer complex [17].

Thermal analysis is done for undoped and doped anthracene using the instrument Perkin Elmer and is shown in Fig. 5. The thermogram of pure anthracene shows a maximum weight loss at 217°C which corresponds to its melting point, whereas H_2Pc doped anthracene crystal undergoes a maximum weight loss at 206°C. However the initial weight loss for the H_2Pc doped anthracene is observed around 195°C. It is understood that due to doping of anthracene by H_2Pc the melting point of anthracene is reduced. Finally conductivity studies were also carried out on pure and doped anthracene crystals and are shown in Fig. 6. Current vs Field for anthracene and H_2Pc doped anthracene crystal shows that both dark as well as photocurrent increases due to doping of H_2Pc. The current obtained for pure H_2Pc crystal is of the order of 10^{-11} A which is not shown in the plot. The results obtained are in good agreement with our earlier findings [9] that conductivity of anthracene increases when it is doped with H_2Pc (Doping in this case might be lowering the band gap). The resistance of the material is very high (order of 10^{12}) and hence the noise current is assumed to be negligible. Due to high resistivity of the organic materials under investigation, the potential inaccuracy due to contact resistance is negligible [18].

5. Conclusion

Though the furnace has been designed for a specific purpose, there are many other combinations of doping possible using this furnace even if they have a wide difference in the melting point or decompose without melting. An attempt has been made to remove the hurdle in growing a doped crystal between substances of varying melting points and it is achieved by the construction of this apparatus. This paves the way for selecting any two materials for the combined growth with an objective for a particular application in the field of medicine, science and technology etc. Recently Matsumoto [19, 20] and his co-workers have reported on the growth of a combined crystal InAs-GaAs as a binary semiconductor for space research application. Phthalocyanine doped anthracene crystal is grown using this newly constructed furnace and characterised by XRD, IR and TGA. As the preliminary experiments on the sample show that doped crystal is photoconducting, the crystals will be analysed for its possible application in the field of semiconductor based solar cell.

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