Investigation on characterization of picric acid doped ADP crystals

J.Velins Stanly[1], C.Muthukrishnan[2], P.Selvarajan[3]
[1]Research Scholar, Reg.No. 7787, Department of Physics, S.T. Hindu College,
Nagarcoil-627010, Tamilnadu, India
(Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli-627012, Tamilnadu, India)
[2]Associate Professor, Department of Physics, KGS College of Arts and Science,
Srivaikundam-628601, Tamilnadu, India
[3]Associate Professor, Department of Physics, Aditanar College of Arts and Science,
Tiruchendur-628216, Tamilnadu, India

Received: June 28 , 2018 Accepted: August 04, 2018

ABSTRACT *Like potassium dihydrogen phosphate (KDP), Ammonium dihydrogen phosphate (ADP) crystal is a nonlinear optical (NLO) material and it finds applications in optical communication, optical storage devices, optical computing and opto-electronics. Detailed research works on undoped and organic and inorganic doped ADP crystals have been carried out by many researchers. Since the work on picric acid doped ADP (PAADP) crystal has been not reported in the literature, the same crystal was grown and studied in this work. Picric acid doped ADP crystals were grown by slow evaporation technique. The harvested crystals of PAADP were characterized by XRD studies, SHG studies, UV-visible spectral studies, microhardness studies, photoluminescence studies, TG/DTA studies, EDAX studies and the results are discussed.*

Keywords: *Single crystal; ADP; doping; growth from solution; characterization; XRD; spectroscopy; hardness; TG/DTA; photoluminescence; EDAX; SHG*

1. Introduction

Ammonium dihydrogen phosphate (ADP) is an isomorphs crystal and it a hydrogen bonded material like KDP. It has some useful physical properties like piezoelectric, ferroelectric, NLO and electro-optic properties. ADP crystal has also other important properties such as broad transparency range, high optical damage threshold and high thermal properties [1-3]. Many researchers have grown and studied varieties of doptants like organics and metals added ADP crystals and the results obtained from the various studies have been reported in the literature [4-8]. L-alanine doped ADP crystals and the properties like optical and electrical properties of the grown crystals have been studied by Akhtar *et al*. [9]. Pattanaboonmee *et al.* have studied the effect of L-arginine on the properties of ADP crystals[10]. Hasmuddin *et al.* have carried out structural, optical, electrical and hardness studies of L-proline doped ADP crystals [11]. Picric acid is an organic yellow crystalline solid, soluble in water, alcohol, chloroform and ether. The presence of three electron withdrawing nitro groups in the picric acid makes it as a good acceptor for neutral carrier donor molecule. Many picrate-type crystals have been grown and studied by many researchers [12-16]. Picric acid has large dipole moment and hence it can increase the NLO property of the host material. In this work, picric acid, an organic dopant, is considered to modify the properties of ADP crystals and various studies of picric acid doped ADP crystals are reported herein.

2. Crystal growth

Initially, picric acid doped ADP (PAADP) sample was synthesized by adding 1 mole% of picric acid into the aqueous solution of ADP. The solution was heated at 50 ^{o}C for 12 hours to get the PAADP salt. The synthesized salt of PAADP was dissolved in double distilled water to prepare the saturated solution and it was stirred and filtered using the good quality filter papers. The filtered solution was taken in a borosil beaker covered with a perforated sheet for slow evaporation. To maintain temperature of the solution constant, the growth vessel was loaded into a constant temperature bath. Due to slow evaporation, initially some speck of crystal nuclei were formed after 5 days. Then, the speck of nuclei grew into big-sized crystals after the solvent evaporated from the solution after a growth period of 25 days. The grown crystal of PAADP is shown in the figure 1. The grown crystal is observed to be slightly yellow colored and transparent.

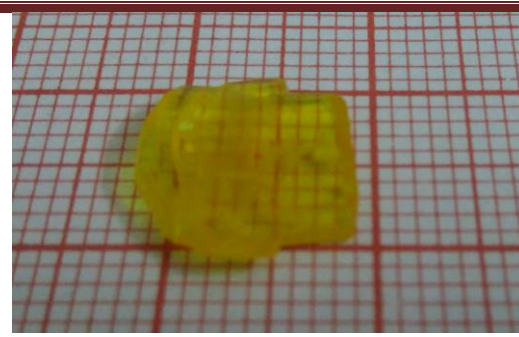

Fig.1: The harvested crystal PAADP

3.Results and discussion

3.1 Identifying the functional groups of the sample

The functional groups of the PAADP crystal were identified by recording the FTIR spectrum using a Perkin-Elmer FTIR spectrometer in the wave number range 400-4000 cm^{-1} using the KBr pellet technique. The recorded FTIR spectrum of the sample is presented in the figure 2. The broad peak around 3250 cm^{-1} is corresponding to the OH stretching vibration of the sample. The absorption peak at 2363 cm^{-1} is due to P-O-H stretching vibration and the strong peak at 1628 cm^{-1} is corresponding to O=P-OH stretching and the absorption peak at 1564 cm^{-1} is due to OH bending vibration. The vibrational peak at 1083 cm^{-1} is due to P=O stretching vibration. The peak at 544 cm^{-1} is due to HO-P-OH bending vibration. The other vibrational peaks in the spectrum are attributed to the presence of picric acid as the dopant in the host ADP crystal. The FTIR spectral assignments for PAADP crystal are given in accordance with the data reported in the literature [17,18]

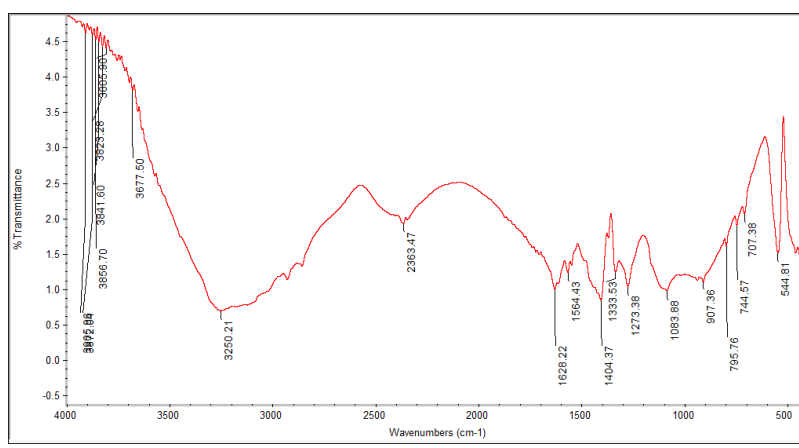

Fig.2: FTIR spectrum of picric acid doped ammonium dihydrogen phosphate crystal

3.2 Thermal studies

Thermal studies like TG/DTA studies are used to identify melting point, decomposition point, exothermic and endothermic transitions of the samples. In this work, TG/DTA thermal curves were recorded using a thermal analyser in the temperature 35 - 600 ^oC in the nitrogen atmosphere. The recorded TG/DTA curves for picric acid doped ADP crystal are shown in the figure 3. From TG thermal curve, there is a slight weight loss observed in the temperature range 150-200 ^oC and this is due to removal of moisture or free water molecules from the sample. In this temperature range nearly 1 weight% of the sample is lost. The endothermic peak at 203 ^oC is corresponding to the decomposition/melting point of PAADP crystal. About 20% of weight is lost 200-300 ^oC and in total about 35% of weight of the sample is observed to be lost at 600 ^oC. After the decomposition of the sample, the broad exothermic transition is noticed in the DTA curve and it corresponds to the emission of gaseous particles from the sample. From the literature, it is observed that the decomposition/melting point of undoped ADP crystal 194 ^oC [19]. Hence, the melting/decomposition point of PAADP crystal at 203 ^oC is found to be more than the undoped ADP crystal and thermal stability is enhanced. This increase of thermal stability of the host ADP crystal is due incorporation of picric acid in the form of ions in the interstitial positions of the lattice of the sample.

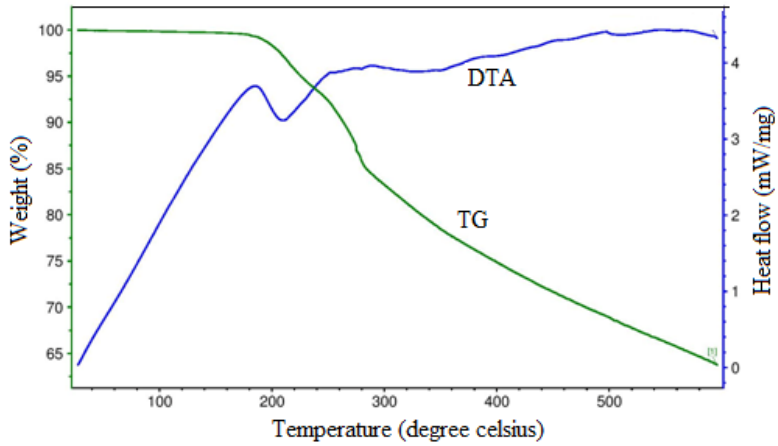

Fig. 3: TG/DTA curves for picric acid doped ADP crystal

3.3 Measurement of hardness

Hardness of a material is the resistance offered to indentation by a much harder body and it may be termed as a measure of the resistance against lattice destruction or the resistance offered to permanent deformation or damage. Microhardness study of the crystals brings out an understanding of hardness, work hardening coefficient and other mechanical parameters. Measurement of hardness is a technique in which a crystal is subjected to a relatively high pressure within a localized area. By suitable choice of a indenter and relatively simple equipment construction, hardness tests can be easily carried out on all crystalline materials under various conditions of temperature and pressure. Vickers microhardness indentations were carried out on the grown crystal at room temperature with the load ranging from 25 g to 100 g using Leitz pyramidal hardness tester fitted with a diamond pyramidal indenter. Vickers microhardness number (H_v) can be calculated using the relation $H_v = 1.8544\ P/\ d^2$ where P is the load in kilograms, d is the diagonal length of indentation impression in mm and 1.8544 is a constant of a geometrical factor for the diamond pyramidal indenter. The obtained values of hardness for undoped ADP and PAADP crystals are given in the figure 4. From the results of microhardness studies, it is observed that hardness number (H_v) increases with load for the samples and this can be explained on the basis of depth of penetration of the indenter. When the load increases, a few surface layers are penetrated initially and then inner surface layers are penetrated by the indenter with increase in the load. The measured hardness is the characteristics of these layers and the increase in the hardness number is due to the overall effect on the surface and inner layers of the sample. For the picric acid doped ADP crystal, the hardness number is found to be increasing. When picric acid is added as dopant into ADP crystal, it may be possible that the strength of bonding improved and this leads to increase of hardness in the doped ADP crystal.

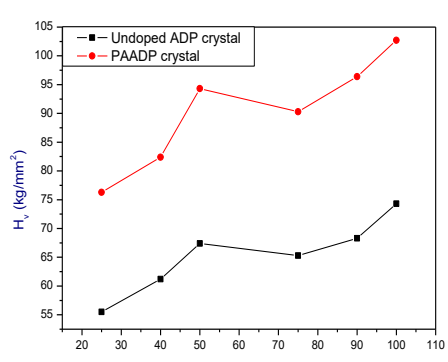

Fig.4. Variation of microhardness with the applied load for PAADP crystal

3.4 EDAX studies

Energy Dispersive Analysis by X-rays (EDAX) or energy dispersive spectroscopy is a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM). This technique

detects X-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. The data generated by EDAX analysis consist of spectra showing peaks; corresponding to the elements making up the true composition of the sample being analyzed. When the sample is bombarded by the SEM's electron beam, electrons are ejected from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from a higher state, and an X-ray is emitted to balance the energy difference between the two electrons states. The X-ray energy is characteristic of the element from which it was emitted. The EDAX detector measures the relative abundance of emitted X-rays versus their energy. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sample. The sample X-ray energy values from the EDAX spectrum are compared with known characteristic X-ray energy values to determine the presence of an element in the sample. In this work, the EDAX spectrum of PAADP crystal was recorded using a computer controlled scanning electron microscope (Model: HITACHI S-3000H) and it shown in the figure 5. From the spectrum, it is confirmed that the elements such as C, O, N and P present in the grown of PAADP crystal. It is to be noted here that the element H cannot be identified by EDAX method. The presence of the elements like C, O, N in the doped ADP crystal indicates that the dopant picric acid has entered into the lattice of the host ADP crystal.

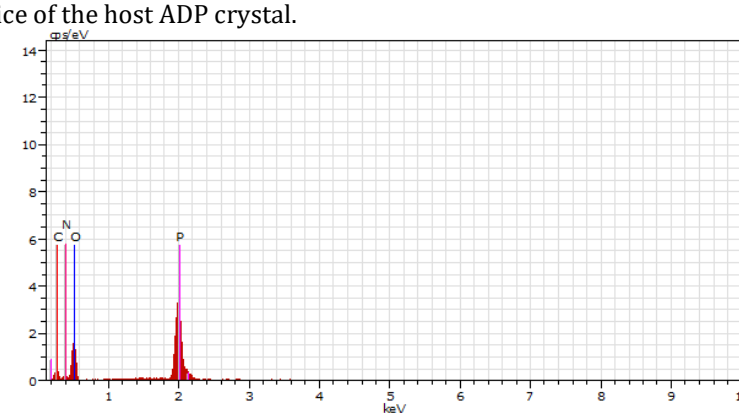

Fig.5. EDAX spectrum of picric acid doped ADP crystal

3.5 Photoluminescence studies

Fluorescence is an optical phenomenon in which, lower wavelength radiation is converted into high wavelength visible radiation. Photoluminescence (PL) measurement is a prominent tool for determining the crystalline quality of a system as well as its exciton fine structure. Photoluminescence in solids is the phenomenonin which electronic states of solids are excited by light of particular energy and the excitation energy is released as light. The photon energies reflect the variety of energy states that are present in the material. The emission PL spectrum of picric acid doped ADP crystal was recorded using a Perkin-Elmer fluorescence spectrometer (Model: LS45) in the wavelength range 200-900 nm. The sample PAADP crystal was excited at 220 nm and the recorded PL spectrum of the sample is shown in the figure 6 and the spectrum consists of three emission bands viz., (i) strong UV emission UV band at 387 nm, (ii) a weak visible band at 518 nm and (iii) a medium IR emission band at 790 nm. Thus, the picric acid doped ADP crystal is the UV, visible and IR emitter when it is excited with 220 nm.

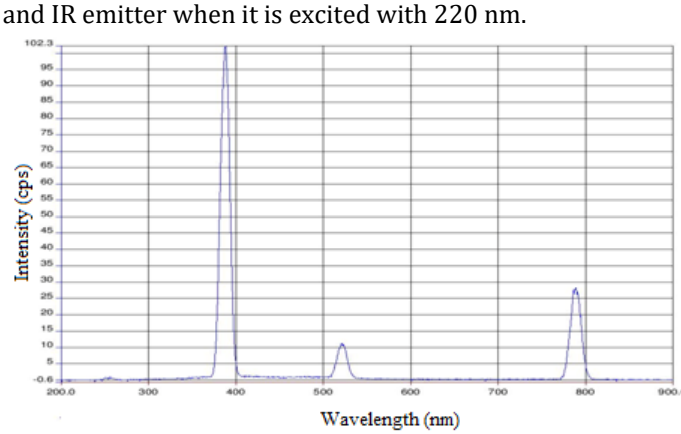

Fig.6. Photoluminescence spectrum of picric acid doped ADP crystal

3.6.Measurement of SHG efficiency

Frequency doubling is also called as the second harmonic generation (SHG) and it was measured using a method known as the Kurtz-Perry technique. The quantitative measurement of the conversion efficiency of the sample can be determined by the modified version of powder technique developed by Kurtz and Perry. The crystal is ground into powder and it is packed densely between two transparent glass slides. Nd:YAG laser is used as the light source and the fundamental laser beam of 1064 nm wavelength, 8 ns pulse in depth with 10 Hz pulse rate is made to fall normally on the sample cell. The power of the incident beam is measured using a power meter and it is 0.68 J/pulse. When the incident laser beam of 1064 nm falls on the sample, the visible laser of wavelength of 532 nm is emitted from the sample and this indicates that the sample PAADP crystal is a second harmonic generator. The transmitted fundamental wave is passed over a monochromator, which separates 532 nm (SHG signal) from 1064 nm and are absorbed by $CuSO_4$ solution. The green light is detected by a photo multiplier tube and displayed on a storage oscilloscope. KDP crystal is powdered to identical size as that of PAADP powdered sample and it is used as the reference material for the SHG measurement. From the experimental data, it is observed that the relative SHG efficiency of PAADP crystal is 2.24 times that of the reference KDP crystal.

3.7 XRD studies

There are two X-ray diffraction (XRD) methods viz., powder XRD and single crystal XRD methods to find the crystal structure and the lattice parameters of crystalline samples. Since the grown PAADP crystal is a single crystal, here single crystal XRD method is used to find lattice constants. Single crystal X-ray diffraction analysis for picric acid doped ADP crystal was carried out using a Bruker Kappa Apex II X- ray diffractrometer with MoK_α radiation (λ= 0.71069 Å). The obtained lattice parameters for PAADP sample are a = b = 7.503 (3) Å, c = 7.579 (2) Å , $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 426.64 (4) $(Å)^3$. From the data, it is confirmed that the grown PAADP crystallizes in tetragonal structure. It is found that the crystal structure of picric acid doped ADP crystal is same as that of undoped ADP crystal [20].

3.8 UV-visible spectral studies

The optical transmission and absorbance spectra of picric acid doped ADP (PAADP) crystal were recorded using a UV-vis-NIR spectrophotometer in the range of 200-900 nm. A good quality crystal of PAADP with a thickness of 1.3 mm was used in this study. The recorded spectra of the sample are shown in the figures 7 and 8. From the absorbance spectrum, it is observed that the absorbance is very low in the visible region and the lower cut-off wavelength is found to be at 470 nm. From the transmittance spectrum, it is noticed that the transmittce is high in the entire visible region. Using the formula $E_g = hc/\lambda$, the optical band gap of the sample is determined and it is found to be 2.642 eV. The sample is yellow in colour and hence the cut-off wavelength is found to be more. Since the absorbance is low in the wavelength range 500-600 nm, this sample can be used as a second harmonic generator and a second order NLO material.

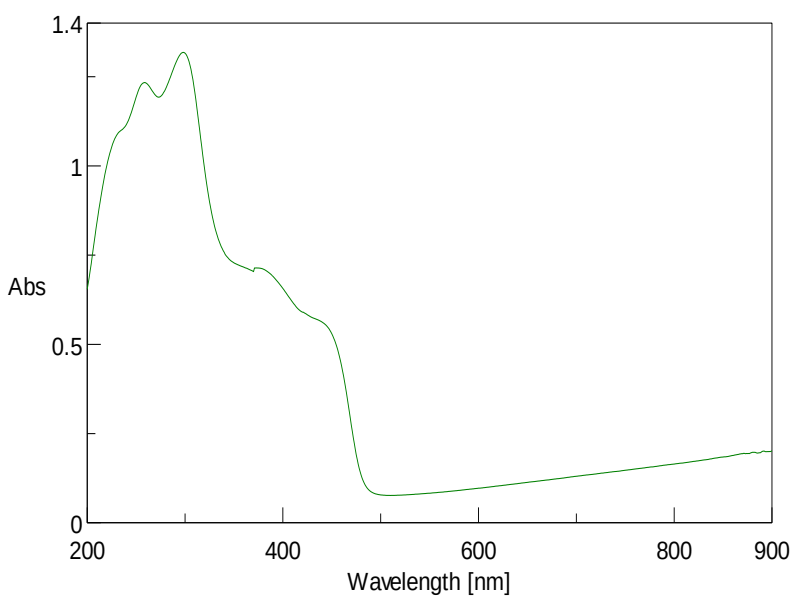

Fig.7. UV-visible absorbance spectrum of PAADP crystal

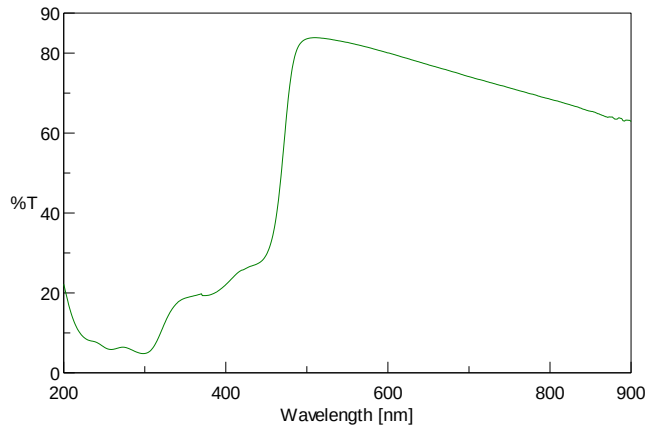

Fig.8. UV-visible transmittance spectrum of PAADP crystal

4.Conclusions

Picric acid doped ADP crystals were grown by solution method at room temperature. The functional groups of the grown crystal were found by FTIR spectral studies. TG/DTA studies reveal that the decomposition point of PAADP crystal is at 203 ^{o}C.The hardness of PAADP crystal is found to be more than that of undoped ADP crystal. The transmittance and absorbance of PAADP crystal were found using UV-visible spectroscopy and the cut-off wavelength of the sample is observed to be at 470 nm. Three photoluminescence peaks at 387 nm, 518 nm and 790 nm are observed from the PL spectrum of the PAADP crystal. SHG efficiency of the grown crystal is found to be 2.24 times that of KDP crystal. The crystal structure of PAADP crystal is observed to be tetragonal like that of undoped ADP crystal.

Acknowledgements

The authors would like to thank the staff members of IIT, Chennai, St.Joseph's College, Trichy, Crescent Eng.College, Chennai, STIC, Cochin University for the help to take the experimental data for the research work.

References

1. Dongli Xu, Dongfeng Xue, J. Crystal Growth 310 (2008) 1385.
2. T. Yokotani, K. Sasaki, C. Yamanaka, Appl. Phys. Lett. 48 (1986) 1030.
3. P. Rajesh, P. Ramasamy, C.K. Mahadevan, J. Cryst. Growth 311 (2009) 1156.
4. N.P. Rajesh, K. Meera, K. Srinivasan, P. Santhana Raghavan, P. Ramasamy, J.Crystal Growth 213 (2000) 389.
5. K. Srinivasan, P. Ramasamy, A. Cantoni, G. Bocelli, Mater. Sci. Eng., B 52 (1998)129.
6. M. Yoshimatsu, Jpn. J. Appl. Phys. 5 (1966) 29.
7. R. Reintjes, E.C. Eckardt, Appl. Phys. Lett. 30 (1977) 91.
8. P. Kumaresan, S. Moorthy Babu, P.M. Anbarasan, Opt. Mater. 30 (2008) 1361.
9. Akhtar Ferdousi, Podder Jiban, J.Cryst.ProcessTechnol2011;1:18–25.
10. N.Pattanaboonmee, P.Ramasamy, R.Yimnirun, P.Manyum, J. Crystal Growth, 314(2011)196–201.
11. Hasmuddin Mohd, Singh Preeti, Shkir Mohd, Abdullah M M, Vijayan N, Bhagavannarayana G, Spectrochim Acta A 123(2014) 376–384.
12. T.Dhanabal, G.Amirthaganesan, M.Dhandapani, Samar K Das, J.Chem. Sci., 124 (2012)91- 96.
13. T. Uma Devi, N. Lawrence, R. Ramesh Babu, K. Ramamurthi, J.Crystal Growth, 310 (2008) 116–123.
14. Mohd. Shkir, B. Riscob, G. Bhagavannarayana, Solid state sciences, 14 (2012)773-776.
15. S. Anandhi , T.S.Shyju, T.P.Srinivasan , R.Gopalakrishnan, J.Crystal Growth, 335 (2011)75–83.
16. D. Shanthi, P. Selvarajan, S. Perumal, Optik, 127 (2016) 3192–3199.
17. P.M. Anbarasan, P. Kumaresan, S. Moorthy Babu, J.Optoelectron. Adv. Mater. 9 (2007) 1299.
18. S. Nirmala Sri Devi, E.K. Girija, Optik, 164 (2018) 498.
19. Mohd. Hasmuddin, Preeti Singh, Mohd. Shkir, M.M. Abdullah, N. Vijayan, V. Ganesh, M.A. Wahab, Mater.Chem.Phys.144 (2014) 293-300.
20. R.W.G. Wyckoff, Crystal Structure, second ed., Interscience, New York(1960).