Studies on the Optical, Mechanical and Dielectric Properties of Nonlinear Optical Single Crystal Bis (Guanidinium) Hydrogen Phosphate Monohydrate (G2HP)

K. Russel Raj and P. Murugakoothan*

PG and Research Department of Physics, Pachaiyappa's College, Chennai – 600 030, India

***Corresponding Author:** murugakoothan03@yahoo.co.in

Abstract— Single crystals of nonlinear optical material bis (guanidinium) hydrogen phosphate monohydrate (G2HP) belonging to non centrosymmetric space group $P\bar{4}2_1c$ were successfully grown by the slow evaporation method. Optical transmittance and second harmonic generation of the grown crystals have been studied by UV-vis-NIR spectrum and Kurtz powder technique respectively. The transmittance of G2HP crystal has been used to calculate the refractive index (*n*), the extinction coefficient (*k*), reflectance (R) and both the real (ε_r) and imaginary (ε_i) components of the dielectric constant as a function of wavelength. The anisotropic mechanical behavior and dielectric response of G2HP has been analyzed.

KEYWORDS: single crystal growth, optical properties, hardness.

1. INTRODUCTION

Nonlinear optical (NLO) materials which can generate highly efficient second harmonic blue-violet light are of great interest for various applications including optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reactions, laser remote sensing, color display, medical diagnostics, etc. In this context, amino acids are interesting materials for NLO applications [1].

Guanidinium family complexes have been chosen for study as potential material for non-linear optics (NLO). Guanidine is an important compound that has many biological, chemical and medical applications [2]. Guanidine as well biguanide, can be employed in material engineering of a promising class of NLO compounds based on salts combining a cation derived from a polarizable organic molecule with an anion capable of forming hydrogen-bonded crystal structures [3].

The crystals display interesting physical and chemical properties, exhibiting phase transitions with ferroelectric, antiferroelectric and ferroelastic behaviors. It is assumed that the organic cations in these salts are mainly responsible for the NLO properties of the crystals. The anionic part (inorganic or organic) of these materials can prevent cations from forming unfavorable centrosymmetric arrangements and are also responsible for favorable chemical, mechanical and thermal properties, due to strong hydrogen bond interactions, which stabilize the crystal lattice [4] and also contribute to the NLO properties of the materials [5].

Among nonlinear optical crystals, organic salts occupy an intermediate position between molecular organic compounds with covalent bonds and inorganic compounds with mainly ionic bonds [6]. The ability of guanidium ion, $[C(NH_2)_3]^+$ in making hydrogen bonds and its unique planar shape has been recognized by Terao *et al.* [7]. Further, the guanidium ions tend to undergo reorientation motions about their (pseudo) C_3 axes in the crystals.

Guanidine is a strong Lewis base and the guanidinium cation may be easily anchored onto numerous inorganic and organic anions and polyanions, largely because of the presence of six potential donor sites for hydrogen-bonding interactions.

Also, inorganic-organic hybrid materials are of great interest in solid state chemistry due to their enormous variety of intriguing structural topologies and their fascinating properties as well as great potential applications in many fields Tao *et al.* [8]. Ammonium dihydrogen phosphate (ADP) is one such inorganic compound, widely used as the second, third, fourth harmonic generator for Nd:YAG and Nd:YLF lasers [9], effectively coordinated with guanidine to form bis (guanidinium) hydrogen phosphate monohydrate denoted as (G2HP).

From the point of view of their physical properties, guanidine compounds are potentially interesting for non-linear optical applications since guanidinium, a polarizable acentric two-dimensional cation, can be regarded as a planar octupolar chemical entity Zyss *et al.* [10]. In the present investigation, attempt has been made to grow single crystals of bis (guanidinium) hydrogen phosphate monohydrate by slow evaporation method. The second harmonic generation property of the crystal has been tested. The grown crystals are subjected to single crystal XRD, liner and nonlinear optical, mechanical and dielectric studies.

I. GROWTH PROCEDURE

The pure bis (guanidinium) hydrogen phosphate monohydrate has been synthesized from an aqueous solution containing Guanidine carbonate (Himedia) and ammonium dihydrogen orthophosphate (Merck) in 1:2 stoichiometric ratios by slow evaporation technique at room temperature. The reaction is as follows,

$$C_2H_{12}N_6.CO_3+2[(NH_4).H_2PO_4]\rightarrow C_2H_{12}N_6.HPO_4.H_2O+(NH_4)_2.HPO_4+CO_2$$

The synthesized G2HP salt is recrystallized several times to improve its purity. The G2HP crystals are grown from the recrystallized saturated solution. The seed crystals are obtained in a period of 3 days using slow evaporation method. Bulk crystals are grown from the saturated solution of G2HP, in a crystallizer, using submerged seed solution slow evaporation method. Crystals of size 32 x 3 x 3 mm^3 are obtained in a period of 20 days and the grown crystal and its morphology are shown in Figs. 1(a) and (b). The crystal growth rate and quality of the crystals are good when the pH is maintained at 7.

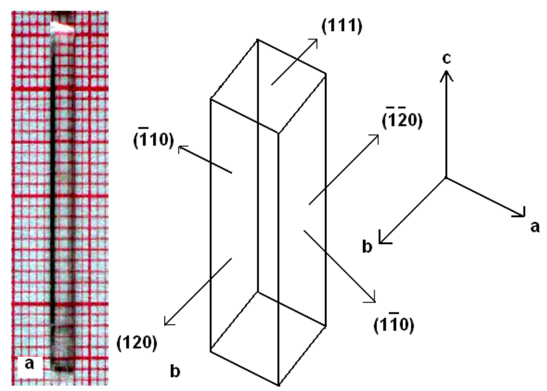

Fig. 1: (a) Single crystal of G2HP, as grown and (b). Morphology of G2HP.

II. CHARACTERIZATION

In order to determine the crystal structure and morphology of G2HP crystals, single crystal X–ray diffraction studies have been carried out using Enraf Nonius CAD4 diffractometer with MoKa (λ=0.7170 Å). The optical absorption spectra for G2HP single crystal has been recorded in the region 200–1400 nm using Varian Carry SE model spectrometer to study their transmission behavior to electromagnetic radiation. The second harmonic generation (SHG) test on the G2HP crystal has been performed by the Kurtz and Perry powder SHG method [11]. The microhardness of the G2HP crystal has been measured using the Reichert MD 4000E ultra microhardness tester fitted with a Vickers diamond Pyramidal indenter attached to a Reichert Polyvar 2 MET microscope. The dielectric studies on G2HP single crystals have been carried out using a HIOCKI 3532 LCR HITESTER instrument. The silver paint coated sample is packed between the copper electrodes and thus a parallel plate capacitor has been formed. The capacitance of the sample is measured by varying the frequency from 100 Hz to 5 MHz.

III. RESULTS AND DISCUSSIONS

A. *Single Crystal X-ray Diffraction and SHG Efficiency*

From the single crystal X-ray diffraction analysis, the lattice parameters of G2HP crystal has been calculated by least square refinement of 25 reflections in the range of 20–30 °. The determined unit cell parameters are presented in Table 1, in comparison with reported [12] and it shows that they are in close agreement.

TABLE 1 LATTICES PARAMETER VALUES FOR G2HP

Powder XRD	Single crystal XRD	Reported [7]
a=b= 16.833 (8)Å	a=b= 16.801 (3) Å	a=b= 16.811 Å
c=7.272 (2)Å	c=7.243 (2) Å	c=7.245 Å
V=2060 Å^3	V=2049 Å^3	V=2049Å^3

Kurtz and Perry second harmonic generation (SHG) test was performed to measure the NLO efficiency of the grown G2HP single crystal. Because the SHG efficiency has been shown to depend on the particle size, crystals of G2HP was grounded separately and sieved into uniform particle size of the order of 150 μm which was tightly packed in separate micro capillary tube of uniform diameter (1.5 mm).the powdered crystalline sample was illuminated using Spectra Physics Quanta ray DHS-2, Nd-YAG laser using the first harmonic output of 1064 nm with pulse width of 8 ns and repetition rate of 10 Hz. The same size KDP sample was used as the reference material. The second harmonic signal generated in the crystalline sample was confirmed by the emission of green radiation (λ=532 nm) from the G2HP crystal. The second harmonic signal of 90 mV/pulse was obtained, while the standard KDP crystal gave a SHG signal of 75 mV/pulse for the input energy. In the powder sample used, the sample crystallites were oriented in different directions. The efficiency of the frequency conversion will vary with the particle size and orientation of crystallites in the capillary tube. From the SHG test, the relative SHG efficiency of the grown G2HP crystal was found to be 1.2 times greater than that of KDP crystal. Higher efficiencies may be expected to be achieved with single crystals by optimizing phase matching.

B. *Optical Studies*

The optical transmission range, transparency cut-off and absorbance band are the most important optical parameters for laser frequency conversion applications. To find the transmission range of G2HP, the optical transmission spectrum is observed for the wavelength between 200 to 1400 nm Fig. 2(a). A crystal of thickness 2 mm is used for this measurement. G2HP is optically transparent in the entire visible region with 85 % transmittance level and lower cut-off wavelength 223 nm which is sufficient for SHG laser radiation of 1064 nm or other applications in the blue region.

The measured transmittance (*T*) is used to calculate the absorption coefficient (α) using the formula [2]:

$$\alpha = \frac{2.303\log\left(1/T\right)}{t} \tag{1}$$

where *t* is the thickness of the sample.

The optical band gap (E_g) is evaluated from the transmission spectra and the optical absorption coefficient (α) near the absorption edge is given by [13]:

$$\alpha h\nu = A\left(h\nu - E_g\right)^{1/2} \tag{2}$$

where *A* is a constant, E_g the optical band gap, *h* the plank's constant and *ν* the frequency of the incident photons. The optical properties of the crystals are governed by the interaction between the crystal and the electric and magnetic fields of the electromagnetic waves. Extinction coefficient is the fraction of light lost due to scattering and absorption per unit distance in a participating medium. In electromagnetic terms, the extinction coefficient can be explained as the decay or damping of the amplitude of incident electric and magnetic fields. The extinction coefficient (*K*) shown in Fig. 2(b), can be obtained from the equation [14]:

$$\mathrm{k} = \frac{\lambda \alpha}{4\pi} \tag{3}$$

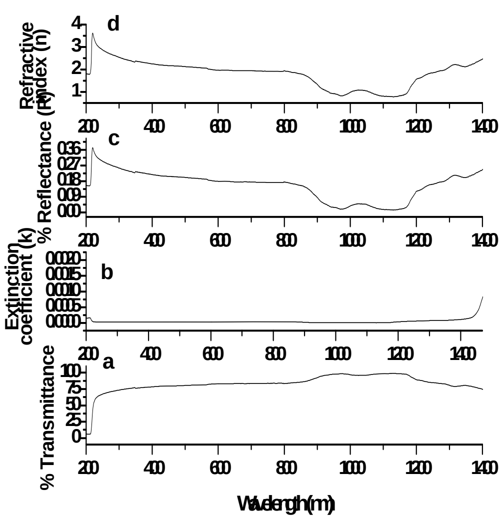

Fig. 2 Spectra of (a) refractive index (*n*), (b) reflectance (*R*), (c) extinction coefficient (k), and (d) transmittance (*T*),

The transmittance (*T*) is given by the following relation [15]:

$$T = \frac{(1-R)^2 \, \mathrm{e}^{-\alpha t}}{1 - R^2 \, \mathrm{e}^{-\alpha t}} \tag{4}$$

The reflectance (*R*) in terms of the absorption coefficient can be obtained from the equation [16]:

$$R = \frac{\mathrm{e}^{-\alpha t} \pm \sqrt{T\,\mathrm{e}^{-\alpha t} - T\,\mathrm{e}^{-3\alpha t} + T^2\,\mathrm{e}^{-2\alpha t}}}{\mathrm{e}^{-\alpha t} + T\,\mathrm{e}^{-2\alpha t}} \tag{5}$$

The refractive index of the material is the most important property of any optical system that uses refraction. It is used to calculate the focusing power of lenses, and the dispersive power of the prisms. The refractive index (n) can be determined from reflectance data using the following relation [16]:

$$n = \frac{-(R+1) \pm 2\sqrt{R}}{R-1} \tag{6}$$

The wavelength dependence reflectance (R) for G2HP crystal and refractive index (n) in the range 200 – 1400 nm are shown in Fig. 2 (c) and 2 (d). Reflectance and refractive index are interdependent on wavelength. The amount of light reflected from the material under normal incidence is proportional to the square of the index change at the face [17]:

$$R = \frac{(n_1 - n_2)^2 + \mathrm{k}^2}{(n_1 + n_2)^2 + \mathrm{k}^2} \tag{7}$$

Initially the refractive index decreases with increasing wavelength, then becomes constant. The average refractive index (*n*) for G2HP crystal is found to be 1.47 for wavelength range between 400-1000 nm. From the optical constants, the electric susceptibility (χ_c) can be calculated using the following relation [18]:

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_c = n^2 - \mathrm{k}^2 \tag{8}$$

Hence

$$\chi_c = \frac{n^2 - \mathrm{k}^2 - \varepsilon_0}{4\pi} \tag{9}$$

where ε_0 is the dielectric constant in the absence of any contribution from free carriers. The value of electrical susceptibility is 0.179 at λ=1000 nm.

The real part of dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the following the relation [19]:

$$\varepsilon_r = n^2 - \mathrm{k}^2 \quad \text{and} \quad \varepsilon_i = 2n\mathrm{k} \tag{10}$$

The value of real ε_r and imaginary ε_i dielectric constant, at 1000 nm are 2.25 and 2.752×10^{-5}, respectively.

The Tauc's graph [20] plotted between the product of absorption coefficient and the incident photon energy $(\alpha h\nu)^2$ with the photon energy ($h\nu$) at room temperature shows a linear behavior that can be considered as evidence of the direct transition. The optical band gap (E_g) of G2HP crystal has been estimated by extrapolation of the linear portion near the onset of absorption edge to the energy axis [21]. From the Fig. 3, value of optical band gap energy of G2HP crystal is found to be 4.94 eV.

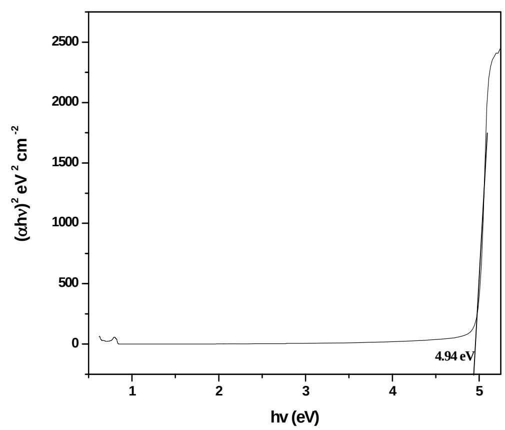

Fig. 3: Variation of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$)

C. *Mechanical Analysis*

Hardness of the material is a measure of resistance it offers to the local deformation [22]. The structure and composition of the crystalline solids are inviolably related to the mechanical hardness. Microhardness testing is one of the best methods of understanding the mechanical properties of the materials such as fracture behavior, yield strength, brittleness index and temperature of cracking [23, 24]. The hardness measurements for G2HP crystal have been carried out on the prominent (120) and (-110) plane of the crystal of thickness 3 mm using Reichert Polyvar 2 MET microscope. The microhardness value is calculated using the following relation [25]:

$$H_v = \frac{1.8544P}{d^2} \; N/m^2 \tag{11}$$

where H_v is the Vicker's hardness number, P is the applied load and d is the average diagonal length of the indentation mark. Measurement of hardness is a useful non destructive testing method used to determine the applicability of the crystal in the device fabrication. Indentations are made on the (120) and (-110) face of the crystal and the micro hardness measurements have been made for the applied loads varying from 1 to 100 g for the dwell time 3 s. A plot between the hardness number and the load is depicted in Fig. 4.

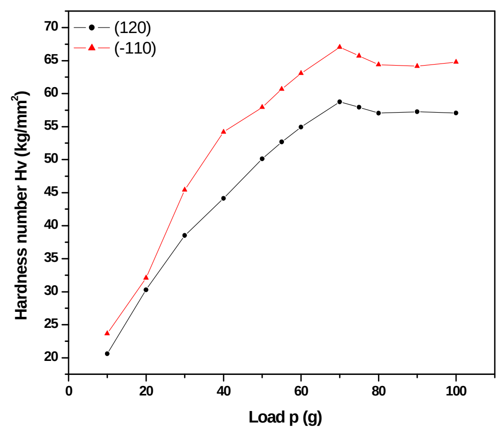

Fig. 4: Vicker's hardness vs. load for G2HP (120) and (-110) planes

We clearly infer that the micro hardness number increases with increasing load. A plot obtained between log (P) and log (d), shown in Fig. 5, gives a straight line. The relation connecting the applied load and diagonal length d of the indenter is given by Meyer's law $P = ad^n$ [26], where the exponent n called as the Meyer's number, is the measure of the indentation size effect (ISE) and a is a constant. The simplest way to describe the ISE is Meyer's law. For the normal ISE behavior, the exponent $n < 2$. When $n > 2$, there is the reverse ISE behavior. When $n = 2$, the hardness is independent of the applied test load, and is given by Kick's law [27, 28].

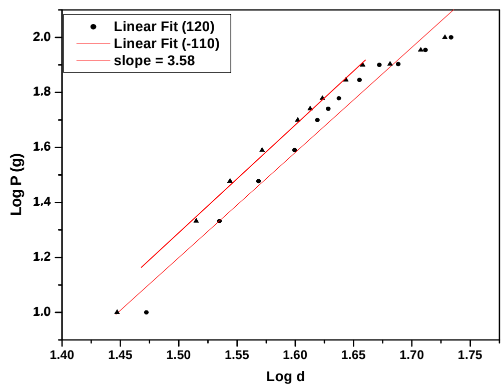

Fig. 5: Variation of Log d vs. Log P for G2HP

TABLE 2 COMPARISON OF STIFFNESS CONSTANT FOR (120), (-110) PLANES OF G2HP

Load (g)	C_{11} ($\times 10^{14}$ Pa) for (120) plane	C_{11} ($\times 10^{14}$ Pa) for (-110) plane
10	199.2653	253.6897
20	390.7692	432.4962
30	595.7658	794.4746
40	755.4704	1082.069
50	944.961	1217.148
55	1030.164	1319.007
60	1108.86	1411.719
65	1247.197	1571.061
70	1216.261	1517.263
75	1183.771	1463.589

The value of n obtained for G2HP crystal in the plane (120) and (-110) using linear fit is found to be 3.58. It is evident from the above plot that the microhardness value of the crystal increases with increase in load is in agreement with the reverse indentation size effect (ISE). [29]. The maximum hardness number obtained on (-110) plane is 58.2 kg/mm^2 at the load of 70 g. But the maximum hardness number found on (120) plane is 67.5 kg/mm^2 at the load of 70 g. This confirms that the grown G2HP crystal exhibits microhardness anisotropy. From careful observations on various materials, Onitsch [30] and Hanneman pointed out that an n lie between 1 and 1.6 for hard materials, and it is more than 1.6 for soft materials. The value of n for the plane (120) and (-110) obtained for G2HP crystals are 3.58 which reveals that the material is soft. The elastic stiffness constant (C_{11}) for different loads are calculated using Wooster's [31] empirical formula $C_{11}=H_v^{7/4}$ is depicted in Table 2, which gives an idea about tightness of bonding between neighboring atoms.

D. *Dielectric Studies*

The cut and polished G2HP single crystal $(10\,mm \times 3\,mm \times 2.2\,mm)$ having silver coating on the opposite faces has been placed between the copper electrodes and thus the parallel plate capacitor is formed. The experiment is carried out for the frequencies from 100 Hz to 5 MHz with the temperatures 30 ºC and 50 ºC respectively. The plot of dielectric constant (ε_r) for different frequency points of G2HP single crystal is shown in figure 6.

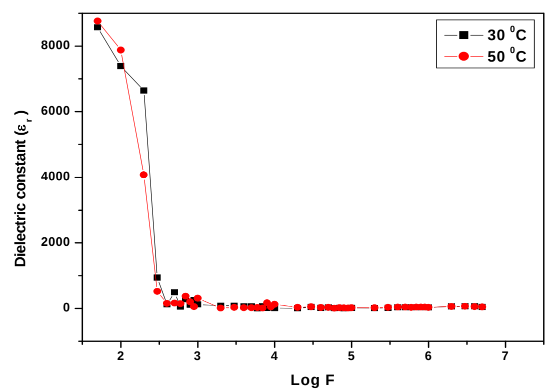

Fig. 6: Variation of dielectric constant vs. Log. of frequency.

The variation of dielectric loss (δ) and capacitance (C) for different frequencies for the grown crystal are shown in Fig. 7(a) and 7(b), respectively.

From the graphs, it is observed that the dielectric constant and dielectric loss decrease slowly with increasing frequency and attains saturation at higher frequencies in all temperatures. The magnitude of dielectric constant of the material depends on the degree of polarization charge displacement in the crystals. At low frequency, dielectric constant depends on the excitation of bound electrons, lattice vibration, dipole orientation and space charge polarization. At low frequencies all the four contributions may be active. The sharp decrease in the values of dielectric constant with the frequency is due to the fact that the frequency of electric charge carriers can not follow the alternation of the ac electric field applied beyond a certain critical frequency [32]. In accordance with Miller rule [33], the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient. It is also observed that both dielectric constant and dielectric loss depend on the temperature and increase with increase of temperature at a constant frequency [34]. Materials with high dielectric constant at low frequency find applications in heating devices [35]. The low dielectric loss at higher frequency region indicates that the grown crystals contain minimum optical defects [36].

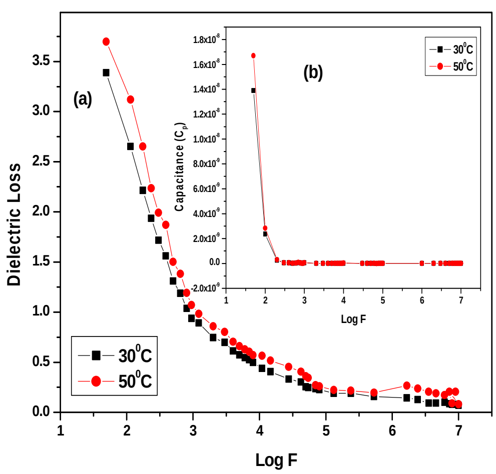

Fig. 7: Variation of (a) dielectric loss and (b) capacitance vs. Log. of frequency

IV. Conclusion

Optical quality single crystals of semiorganic G2HP have been grown using solution growth technique. The grown crystals are observed to be transparent and colorless with well defined rectangular morphology. The unit cell parameter values show that the G2HP single crystal belongs to tetragonal system with non centrosymmetric space group $P\bar{4}2_1c$. Optical studies show that the crystal has wide transmission range with UV cut off wavelength at 223 nm. The optical band gap E_g, absorption coefficient (α), extinction coefficient (k), refractive index (n), reflectance (R) have been calculated as a function of wavelength. The SHG efficiency of the grown crystal in frequency conversion is found to be 1.2 times that of KDP. Hardness measurement shows that G2HP crystal is mechanically stable up to 110 g. The dielectric studies proved that the sample has low dielectric constant and dielectric loss values at higher frequencies for G2HP suggests that the sample possess enhanced optical quality with lesser defects.

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Dr. P. Murugakoothan is an assistant professor of PG and Research Department of Physics of Pachaiyappa’s College, Chennai, India. He has received his B.Sc., MSc., M.Phil. and PhD degrees in Physics, respectively, from T.B.M.L. College of Barathidasan, Pachaiyappa’s College of University of Madras, College of Engineering of Anna University, and Crystal Growth Center of Anna University, India, in years 1985, 1987, 1990, and 1994. His fields of research are Material Science, Crystal Growth, and Nanocrystal. He has been the author/ co-author of 62 national and international journals and 5 books.

K. Russel Raj was born in Edaicode Village, Vilavencode Taluk, Kanyakumari District, Tamilnadu, in 1968. He has received his B.Sc., M.Sc., and M.Phil. degrees in Physics, respectively, from Nesamony Memorial Christian College of Marthandam, Annamalai University, Chidambaram, and Madurai Kamaraj University of Madurai, India, in years 1990, 1993, and 1996. He has joined Ph.D. in Physics in at Pachaiyappa’s College of Chennai, in 2009. Now, he is also a Research Scholar of PG and Research Department of Physics of Pachaiyappa’s College Chennai, India. He has participated/ presented 13 papers in domestic conferences and is the author/ co-author of 10 published papers in reputed international journals.

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