



Research article

Structural, vibrational and optical studies on semiorganic crystals of boric acid potassium acetate

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ARTICLE INFO

Keywords:

Materials chemistry
Analytical chemistry
Powder XRD
FTIR
FTRAMAN
UV - visible
PL
SHG

ABSTRACT

A semiorganic crystal of Boric acid potassium acetate has been grown by low temperature solution growth technique at room temperature using deionized water as a solvent. The crystalline nature of the compound was confirmed by the sharp and well defined peaks observed from the powder X-ray diffraction pattern. By single crystal X-ray diffraction method, the structure of the grown crystal has been studied. The Boric acid Potassium Acetate (BAPA) crystal has good optical transmittance in the entire UV visible region. FT-IR and FT-Raman spectral studies were performed to identify the vibrations of functional groups. The mechanical strength of the grown crystal was determined by Vicker's micro hardness test. Photoluminescence study was carried out on the crystal. The SHG study represents the nonlinear optical efficiency of the crystal.

1. Introduction

Amino acid and their complexes in the family of organic materials have been examined for photonic applications. The photonic crystals did not allow the propagation of light through the band gap, that have enabled exciting new way to control and construct integrated optical devices. Plenty of natural amino acids are individually exhibiting nonlinear optical properties because of a donor NH₂ and an acceptor COOH. In addition to that, intermolecular charge transfer is possible [1].

In the frame of reference, many organic Non Linear Optical (NLO) crystals were investigated. But much attention has been paid towards semiorganic Non Linear Optical (NLO) materials so that they have large non linearity, high resistance, improved chemical stability and good mechanical strength.

Pure inorganic Non Linear Optical (NLO) materials normally have mechanical and thermal properties but possess relatively unpretentious optical nonlinearity because of lack of extended π - electron delocalization.

The aim of boric acid doped with potassium acetate is to enhance the nonlinearity of the crystal. The borate families of the crystal have a good power threshold figure of merit and proved a track record of enhancing the non linear optic nature of crystals [2]. The novel metal organic Non Linear Optical (NLO) material like Dipotassium Boro Maleate, Potassium Boro Succinate, Cesium triborate, Cesium lithium borate, Strontium

boron Beryllium Oxide, Potassium aluminium borate have been synthesized and investigated [3, 4, 5, 6, 7, 8]. One of the important borate is potassium borate which is widely used in metal refining, welding, cement insulation fiber glass and non-linear materials [9]. Non Linear Optical (NLO) material can be utilized for optoelectronic applications such as optical computing, optical communication, optical data storage and electro optic shutters [10, 11, 12, 13, 14]. Majority of optoelectronic devices (direct conversion between electrons and photons) are LEDs, Laser diodes, photo diodes and solar cells.

In the present work, we have made an attempt to semi organic nonlinear crystals of Boric acid with potassium acetate. The grown crystals were subjected to various characterization techniques. The crystal was characterized under various techniques such as Single XRD, Powder XRD, FTIR, FTRAMAN, UV-Visible, PL and SHG.

2. Experimental procedure

2.1. Material synthesis

Boric acid Potassium Acetate (BAPA) crystal was synthesized using Boric acid and Potassium acetate in equal molar ratio 1:1 by slow evaporation method at room temperature. The solution was prepared using deionized water as solvent. The prepared supersaturated solution was dissolved using a magnetic stirrer at a constant speed and filtered.

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The solution was allowed for super nucleation and the crystal was ready for the investigation after 61 days. The photograph of the Boric acid Potassium Acetate (BAPA) crystal is shown in the Figure 1.

3. Results and discussion

3.1. Powder XRD analysis

Powder XRD data of Boric acid Potassium Acetate (BAPA) crystal indicates the pure crystalline nature of the crystal. Figure 2 indicates the P-XRD pattern of the experimental crystal. The values are observed by powder X-ray diffractometer XPERT PRD with $\text{CuK}\alpha$ (1.5425 Å). The sample was in the range 10° – 80° with a scanning rate of 3° per/min. The anode material used in this study was Copper. The sharp and well defined Bragg peaks at specific 2θ value in the powder XRD pattern confirmed its crystallinity. The values obtained from Power XRD pattern for the grown BAPA crystal are given (Table 1).

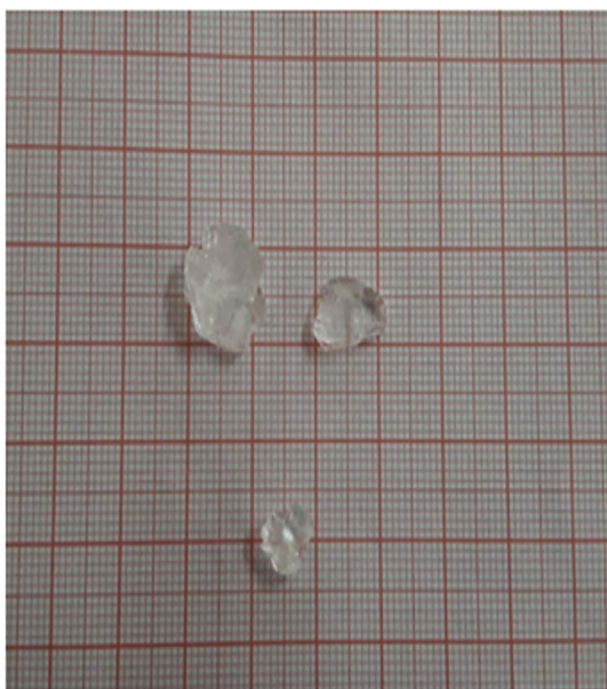


Figure 1. Photograph of BAPA single crystal.

3.2. Single X-Ray diffraction

The grown single crystal Boric acid Potassium Acetate (BAPA) has been subjected to single X-Ray diffraction analysis using an ENRAF NONIOUS CAD-4 automatic X-ray diffractometer with $\text{MoK}\alpha$ radiations ($\lambda = 0.717 \text{ \AA}$), to determine unit cell dimension of Boric acid Potassium Acetate (BAPA). The unit cell parameters are $a = 9.08 \text{ \AA}$, $b = 11.20 \text{ \AA}$, $c = 11.15 \text{ \AA}$ and volume $v = 1139 \text{ \AA}^3$. From the above data, it is clear that Boric acid Potassium Acetate (BAPA) crystal belongs to orthorhombic crystal system (Table 2).

3.3. FTIR and FTRaman vibrational assignments of BAPA

FTIR and FTRAMAN studies are useful for the identification of various functional groups present in the grown crystal. The recorded FTIR and FTRAMAN spectra of Boric acid potassium acetate crystals are depicted

Table 1. XRD spectrum values of the grown BAPA Crystal.

Pos. [2θ .]	Height [cts]	FWHM Left [2θ .]	d-spacing [\AA]	Rel. Int. [%]
14.8464	53.42	0.1476	5.96714	11.58
15.8152	264.35	0.1476	5.60371	57.29
19.5397	32.53	0.2952	4.54317	7.05
25.2725	443.72	0.1968	3.52412	96.17
26.5319	461.39	0.1476	3.35963	100.00
27.1012	92.63	0.1968	3.29032	20.08
30.0743	51.83	0.1476	2.97148	11.23
30.5574	45.05	0.0984	2.92559	9.76
31.6812	36.28	0.2952	2.82434	7.86
32.3049	216.91	0.1476	2.77122	47.01
34.8111	32.06	0.2952	2.57723	6.95
35.6046	72.61	0.1476	2.52160	15.74
37.8142	44.54	0.1968	2.37918	9.65
39.2742	39.95	0.2952	2.29404	8.66
39.8276	24.44	0.2952	2.26343	5.30
41.3937	77.98	0.5904	2.18134	16.90
42.7681	38.24	0.3936	2.11437	8.29
45.1760	16.52	0.7872	2.00712	3.58
48.5926	24.08	0.2952	1.87368	5.22
49.8546	13.71	0.7872	1.82917	2.97
52.6508	15.36	0.2952	1.73843	3.33
54.8011	9.17	0.5904	1.67519	1.99
57.1395	10.96	0.5904	1.61207	2.38
59.8591	14.28	1.1808	1.54517	3.10

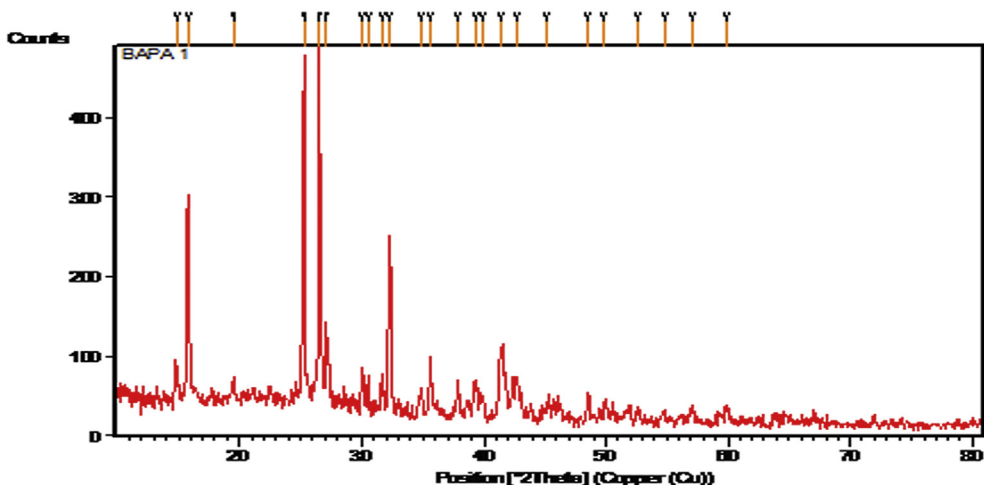


Figure 2. Powder X-ray diffraction spectrum for BAPA.

Table 2. Single XRD data of BAPA.

Crystallographic data	BAPA
a (Å)	9.08
b (Å)	11.20
c (Å)	11.15
α	90
β	90
γ	90
System	Orthorhombic

in the Figures 3 and 4 respectively. The vibrational assignments are given in the Table 3. At 592 cm^{-1} , OBO ring asymmetric bending is identified. OBO ring bending is assigned to 510 cm^{-1} and 455 cm^{-1} . At 1103 cm^{-1} and 1352 cm^{-1} , B–O asymmetric stretching is assigned. In FT-Raman Spectrum, a peak observed at 448 cm^{-1} is due to OBO ring bending. Peaks observed at 3364 cm^{-1} and 3053 cm^{-1} are due to B–OH stretching vibrations [15]. B–O asymmetric stretching is indicated by 1119 cm^{-1} peak. From Table 3, most of the vibrations present in both IR and Raman spectra are almost the same, thus configuring the non-centrosymmetric nature of the crystal.

3.4. UV – visible spectral analysis

UV – visible spectral analysis is used in the recent need for the fabrication of new photonic devices which having highly transparent in a particular region. Figure 5 depicts the transmittance spectrum of Boric acid Potassium Acetate (BAPA) crystal. The UV cut-off wavelength of the grown crystal is observed at 240 nm . Boric acid Potassium Acetate (BAPA) crystal having a broad transmission gap in the region 241 nm – 1100 nm , which shows that Boric acid Potassium Acetate (BAPA) can be used for laser application [16]. The calculated band gap of the crystal is found to be 5.17 eV by using the formula, $E_g = hc/\lambda$.

3.5. Photoluminescence study

Photoluminescence (PL) spectroscopy is one of the powerful tools to provide relatively direct information about the molecular level, as well as shallow, deep level defects and band gap states [17]. The luminescence (PL) spectrum of Boric acid Potassium Acetate (BAPA) is recorded in the range 350 – 600 nm with excitation wavelength of 320 nm at room temperature as shown in the Figure 6. The emission spectrum shows peaks at 360 and 520 nm . The calculated band gap is about 2.3 eV . From that we

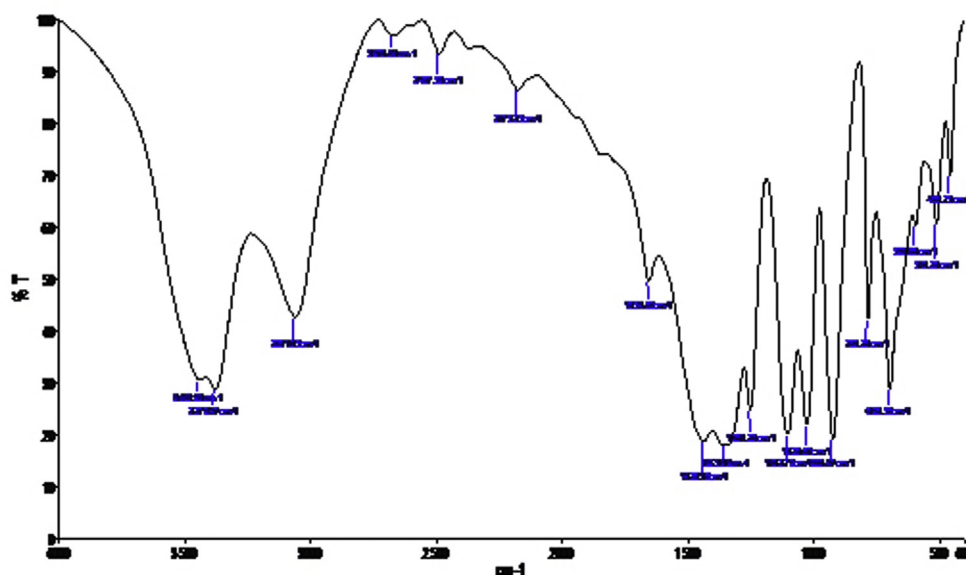
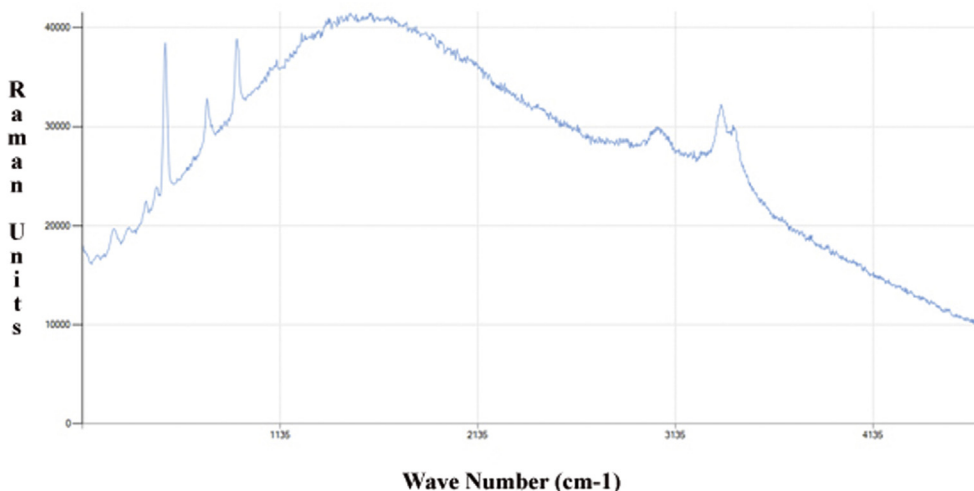
**Figure 3.** FTIR spectrum of BAPA crystal.**Figure 4.** FTRAMAN spectrum of BAPA crystal.

Table 3. FTIR and FTRAMAN Assignments for the grown BAPA crystal.

Wave number (cm ⁻¹)		Assignment
FTIR	FTRAMAN	
3379	3364	B–OH stretching
3061	3053	B–OH stretching
1922	1922	C–H out of plane bending
1352	-	B–O asymmetric stretching
1251	1265	B–O vibrations
1103	1119	B–O asymmetric stretching
1026	-	B–O terminal stretching
782	772	B–O ring stretching
592	552	OBO ring asymmetric bending
510	-	OBO ring bending
455	448	OBO ring bending

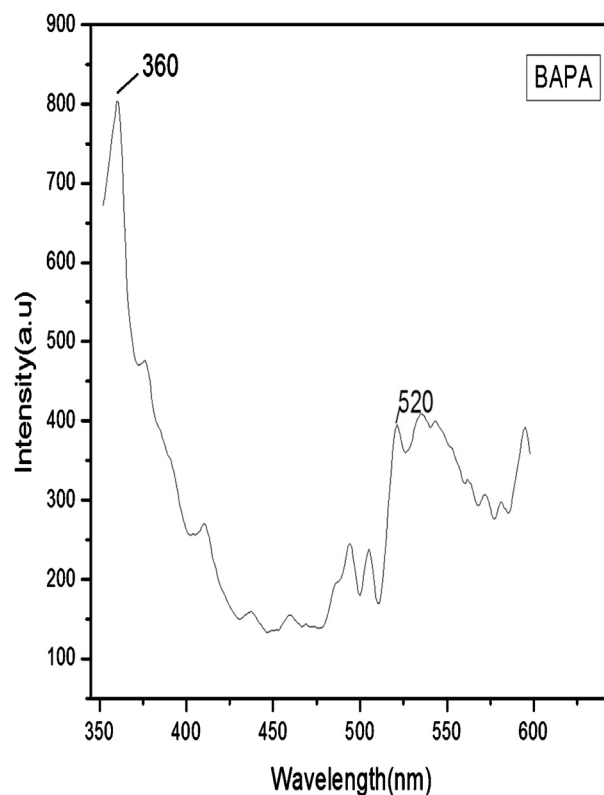
conclude that the material might be suitable for optoelectronic laser devices and UV filters.

3.6. Second harmonic generation study

The second harmonic generation test was achieved by Kurtz and Perry [18]. It is an essential and very popular tool to measure the conversion efficiency of Non Linear Optical (NLO) materials to identify the material with non-centro symmetric crystal structures. The fundamental beam of 1064 nm from Q-switched Nd:YAG laser was used to identify the second harmonic generation (SHG) property of Boric acid Potassium Acetate (BAPA) crystal. Pulse energy 1.2 mJ/pulse and pulse width 8 ns with a repetition rate of 10 Hz were used. The sample of Boric acid Potassium Acetate (BAPA) was made in the powder form. The powdered sample was filled in air tight micro capillary tube of uniform bore about 1.5 mm diameter. Laser was made to fall normally on the sample cell. The input laser beam passed through an IR reflector and directed towards the micro crystalline powdered sample. The SHG radiation of 532 nm (green light) was collected by photo multiplier tube (PMT – Hamamatsu – model R 2059). From that, the SHG relative efficiency of Boric acid Potassium Acetate (BAPA) crystal was found to be 0.09 times higher than that of potassium dihydrogen phosphate (KDP).

3.7. Micro hardness study

Micro hardness measurement of Boric acid Potassium Acetate (BAPA) crystal was carried out using Shimadzu HMV – 2 fitted with Vickers

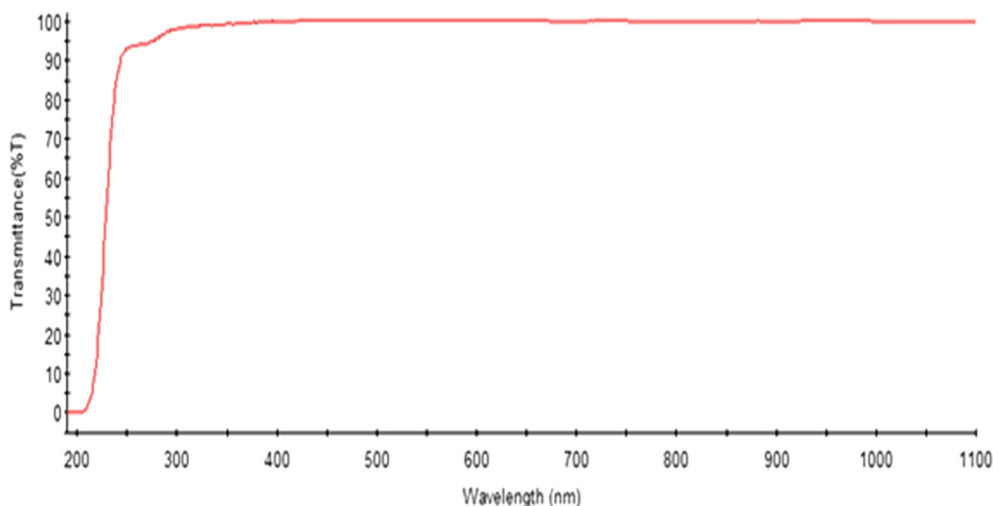
**Figure 6.** Photoluminescence spectrum of BAPA crystal.

pyramidal indenter and connected to an incident light microscope. Generally, the micro hardness measurement is used to determine the mechanical strength of the material. Hardness measurements were taken for applied load varying from 25 to 100 gm.

$$H_v = 1.8544 \frac{p}{d^2} \text{ kg/mm}^2$$

where 'p' is the applied load in kg, 'd' is the diagonal length of the indentation impression in millimetre and 1.8544 is a constant. Well-developed face of grown crystal was selected for micro hardness study.

A graph is plotted between hardness number (H_v) and load (p) as shown in the Figure 7. From the graph, it is found that the hardness value increases with increase of load (Table 4). It reveals that the material has good mechanical strength.

**Figure 5.** Transmittance spectrum of BAPA crystal.

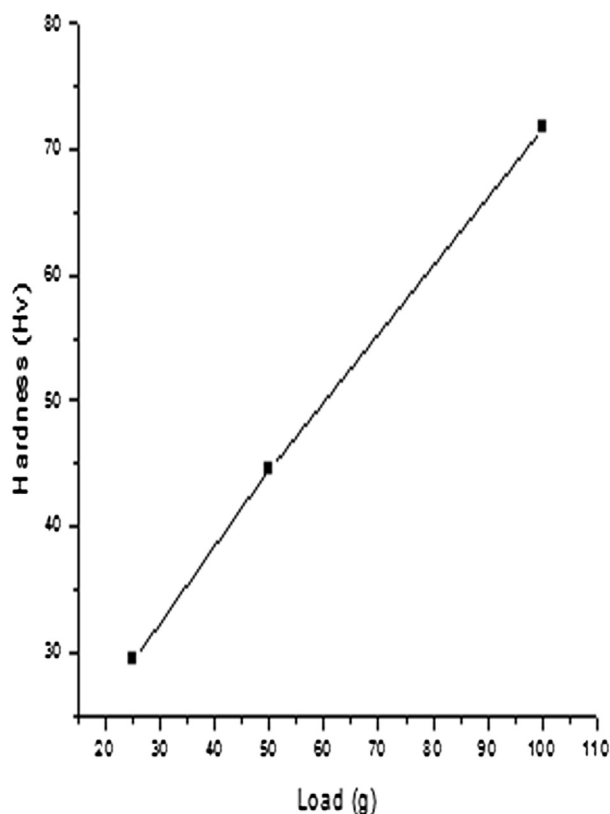


Figure 7. Microhardness graph of BAPA.

Table 4. Microhardness of BAPA crystal.

Load: 25grm			
S. No	L1	L2	HV
1	37.55	41.26	29.8
2	38.29	41.61	29.0
Load: 50grm			
S. No	L1	L2	HV
1	44.32	47.75	44.7
2	44.42	46.70	44.6
Load: 100grm			
S. No	L1	L2	HV
1	48.71	52.52	72.3
2	49.29	52.36	71.0

4. Conclusion

The Boric acid Potassium Acetate (BAPA) single crystals were grown by slow evaporation solution growth technique at room temperature by using deionized water as a solvent. The single crystal was obtained in a period of 61 days. These crystals were subjected into various characterizations. Single crystal X-ray diffraction analysis shows that Boric acid Potassium Acetate (BAPA) crystal belongs to Orthorhombic crystal system with lattice parameter $a = 9.08 \text{ \AA}$, $b = 11.20 \text{ \AA}$, $c = 11.15 \text{ \AA}$ and volume $v = 1139 \text{ \AA}^3$. The powder XRD analysis confirms the crystalline nature of the materials. The presence of various functional groups of Boric acid Potassium Acetate (BAPA) crystals have been confirmed by FTIR, FTRAMAN spectroscopy and thus the non-centro symmetric nature of the crystal was concluded. Good optical transmittance occurs in the

entire visible region and the lower cutoff wavelength is observed at 240 nm. Photoluminescence study was carried out on the crystal and the band energy was about 2.3 eV, so that the material is suitable for optoelectronic laser devices. SHG study confirms that Boric acid Potassium Acetate (BAPA) crystal exhibit the nonlinear optical property. From the micro hardness study of the grown crystal, it is found that the crystal possess good mechanical strength.

Declarations

Author contribution statement

S Anand: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

C. Kayalvizhi, R. Durga: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

B. Samuel Ebinezer: Performed the experiments; Analyzed and interpreted the data.

R. S. Sundararajan: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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