Growth, structural, thermal and dielectric studies of α-glycine single crystals grown under the influence of potassium iodide for nonlinear optical applications

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Abstract

Glycine has the simplest structure among all amino acids. Many attempts have been made to grow different derivative crystals of glycine. However, the title compound was not investigated thoroughly to understand the usability of the crystal for its device application. In the present investigation, using slow evaporation solution growth technique, single crystals of glycine have been grown in the presence of potassium iodide. Detailed investigations were made on structural and thermal properties of the grown crystals. Structural analysis was carried out by X-ray diffraction method, Fourier Transform Infrared, FT-Raman and Nuclear Magnetic Resonance spectral methods to conform the grown crystals. Thermal stability of the grown crystals was studied by Thermogravimetric (TG) and Differential Thermal analysis (DTA) and it was found that the crystal is stable up to 113°C. UV-Vis spectral analysis has been carried out and the crystal has not any significant absorbance in the entire visible region. Dielectric studies for the grown samples have also been studied. Nonlinear optical property has been confirmed by Kurtz powder technique and found that the grown crystal has nearly fifty percentage of SHG efficiency as that of standard KDP sample. The observed properties have confirmed that the grown crystal is suitable for nonlinear optical applications. Copyright © 2017 VBRI Press.

Keywords: Crystal growth, nonlinear optical, X-ray diffraction, FTIR, NMR.

Introduction

The development of potential nonlinear optical crystals, generating blue and green laser is of great interest among the Researchers for the applications of optical data storage, optical amplifiers, image processing, frequency conversion, etc. for the last few decades. Organic nonlinear optical materials (NLO) play a major role in nonlinear optics for the fast processing of information and for data storage applications [**1**]. Organic materials attract much interest to chemists, material scientists and optical physicist because of their superior performance with respect to NLO properties such as the large NLO efficient, ultrafast nonlinear response time, and high optical damage threshold [**2**]. Amino acids and their complexes belong to a family of organic materials that have been considered for photonic applications [**3,4**]. Out of around twenty amino acids glycine is the simplest of all. Glycine family crystals have been subjected to extensive research by several researches for their efficient NLO properties [**5-10**]. Single crystal of γ- glycine was grown in the aqueous solution of ammonium carbonate and the linear and nonlinear optical properties were reported [**11**]. In the presence of sodium sulphate, the γ-glycine single crystal was grown and it's structural, optical, thermal and NLO studies were reported [**12**]. Recently, influence of sodium formate on the growth and characterization of γ- glycine single crystal has been reported by Ezhilvizhi *et al*. [**13**]. Within the scope of our literature survey, it is observed that the glycine crystals were not grown in the presence of potassium iodide. It is expected that the presence of potassium iodide, will suppress the growth of microbes in the solution during the growth period.

Hence, in the present work, an attempt has been made successfully to grow single crystals of glycine in the presence of potassium iodide and found that the grown crystals are α-glycine and a systematic investigation has been carried out on α-glycine single crystal grown in the presence of potassium iodide by slow evaporation solution growth technique. The grown crystals were characterized by single crystal X-ray diffraction method, powder X-ray diffraction method, Fourier Transform Infrared, FT-Raman and Nuclear Magnetic Resonance spectral methods to conform the grown crystals. Thermal stability of the grown crystals was studied by Thermogravimetric (TG) and Differential Thermal analysis (DTA). UV-vis spectral analysis has been carried out to find the absorbance of the grown crystals. Nonlinear optical property has been confirmed by Kurtz powder technique. Dielectric studies for the grown samples have also been studied and reported in this paper.

Experimental

Materials

The chemicals Glycine and potassium iodide used in the present investigation were purchased from SISCO Research lab India and used without further purification.

Crystal growth

Glycine (99% pure) and Potassium Iodide (99% pure) were taken in equimolar 1:1 ratio in excess of deionized water for the growth. The calculated amount of glycine was dissolved in deionized water for one and half hours to get complete dissolution. Then the appropriate amount of Potassium Iodide was added to the solution. The resultant solution was continuously stirred for 3 hours. The homogeneous solution was filtered to avoid impurities if any and transferred to petri dish. This solution was kept in room temperature and allowed to evaporate slowly. After 40 days, a well-developed and optically transparent single crystal with the maximum dimension of 16x8x7 mm^3 was harvested. The grown crystals were tested by various techniques and found that they are α-glycine single crystals and the photograph of as grown single crystals is shown in the inset of **Fig. 1**.

Characterization

The grown crystals were analyzed by various techniques. Single crystal x-ray diffraction study was carried out by using an instrument ENRAF NONIUS CAD -4 MV3 single crystal x-ray diffractometer in order to find the lattice parameters and crystal system. The powder X-ray diffraction analysis was also carried out by using Xpert Pro diffraction system to ensure the crystalline nature. The powder sample prepared from the seed crystals was mixed with KBr in 1:20 weight ratio and made as a pellet to obtain the Fourier transform infrared spectrum of the grown crystal by using BRUKER IFS 66V FTIR spectrometer in order to find the presence of various functional groups. Bruker RFS 27 model FT-Raman spectrometer was used to record the FT- Raman spectrum for the confirmation of functional groups. The Proton NMR spectrum of the sample was recorded using an AMX 400 MHz spectrometer in DMSO-d6 Perkin Elmer to identify the functional group protons. The PL measurements were carried out in Perkin Elmer LS 55 Luminescence spectrometer. Linear optical properties of the crystals were studied by using Elico SL218 double beam UV-Vis Spectrophotometer and nonlinear optical properties were tested by Kurtz Perry powder technique [**14**]. Thermo-gravimetric (TG) and Differential Thermal Analysis (DTA) for the crystal samples were carried out in nitrogen atmosphere by a Thermal Analyzer EXSTAR TG/DTA 6200 model supplied by SII Nanotechnology, Japan to study the thermal properties of the as-grown crystal. The dielectric studies were carried out the conventional parallel plate capacitor method with different frequencies from 1 KHz to 10 KHz at temperature ranges using the Agilent 4284A LCR meter.

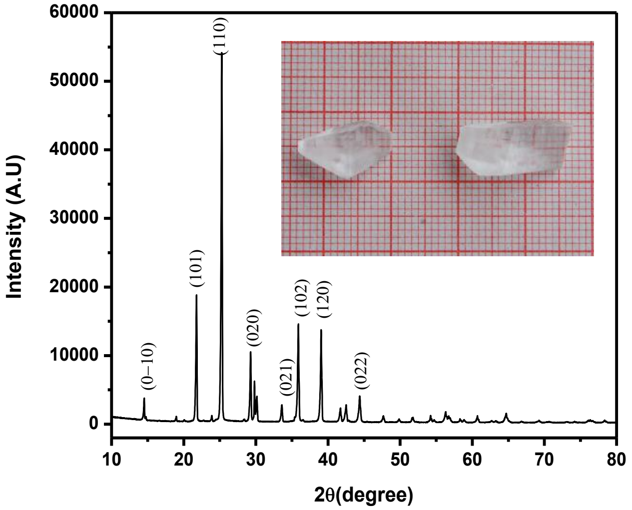

Fig. 1. Powder XRD pattern of α-glycine grown in the presence of potassium iodide and the photograph of as grown crystals is in the inset.

Results and discussion

Structural analyses

X-ray diffraction analyses

Single crystal X–ray diffraction analysis has been carried out to determine the lattice parameters. The data have been collected at 293 K using MoK_{α} (λ = 0.71069 Å) radiation. The grown crystals possess monoclinic structure and the lattice parameter values were determined as a= 5.117 A˚, b=11.997 A˚, c=5.479 A˚ and β=111.68˚. Repeated measurement of lattice parameters was done and confirmed that it has reasonably good agreement with α-glycine [**15**]. In addition to this, the well ground powder of the grown samples of grown crystals was subjected to powder X-ray diffraction (PXRD) analysis with a monochromatic Cu Kα radiation (λ=1.5401 A˚). The data have been collected at 298 K between 10˚ and 80˚ of diffraction angles with the source wavelength of 1.54 A˚. The step size of 2θ and the scan step time were fixed as 0.017° and 10.325 seconds respectively. The sharp diffraction peaks have been observed in the XRD pattern which ensures the good crystalline nature of the grown samples. The d-spacing of the diffraction peaks were calculated using the 2θ value. The diffraction peaks corresponding to different crystal planes were indexed by using the 2θ, and d-spacing for the obtained crystal system in the single crystal x-ray diffraction study. The indexed powder X-ray diffraction (PXRD) pattern of the grown crystalis shown in **Fig. 2**. It is observed that the powder diffraction pattern is reasonably coinciding with the previously reported crystal.

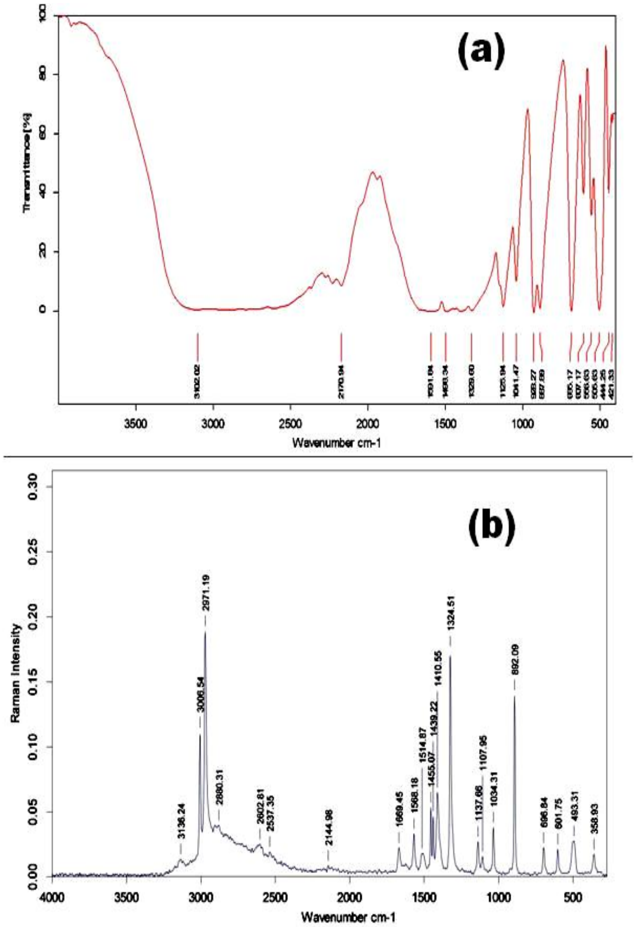

Fig. 2. (a) FTIR spectrum and (b) FT-Raman spectrum of α-glycine grown in the presence of potassium iodide.

FTIR and FT-Raman spectral analyses

Vibrational spectroscopy is an important tool for understanding the chemical bonding and the presence of various functional groups of a material. It also provides evidence for the charge transfer interaction between the donor and acceptor groups through π-electron movement. FT-Raman spectrum will give precise resolved intensities for some unresolved bands in the FTIR spectrum [**4**]. FTIR and FT-Raman spectra have been recorded for the grown crystal from 450-4000 cm^{-1} and 50-4000 cm^{-1} as shown in **Fig. 2 (a) and 2 (b)**, respectively. In the FTIR spectrum of grown crystal sample (**Fig. 2(a)**), the broad absorption band from 2000 to 3500 cm^{-1} include overlap of absorption peaks due to O–H stretch of –COOH and N–H stretch of NH_3^+ of glycine molecule. The CH_2 vibrations which generally lie just below 3000 cm^{-1} are not clearly resolved in the FTIR spectrum. The broad absorption band in the above range is due to the presence of hydrogen bonding [**4, 16**]. The C=O vibration of –COOH lies around 1592 cm^{-1} and the CH_2 bending mode appears at 1329 cm^{-1} in FTIR spectrum. The torsional oscillation of NH_3^+ occurs nearly at 506 cm^{-1}. FT- Raman spectra of the grown crystals have also been obtained to confirm the presence of functional group and shown in **Fig. 2(b)**. Unresolved absorption bands in the FTIR spectra are clearly resolved in the FT- Raman spectra. The observed frequencies and the tentative assignments of the Raman lines in comparison with FTIR vibrations are given in **Table 1**.

Table 1. Important wave numbers observed and their tentative assignments of FTIR and FT-Raman spectra for α-glycine sample.

Wave numbers (cm^{-1})		Assignments
FTIR	**FT-Raman**	
3102	--	N – H symmetric stretching
--	3136	N – H symmetric stretching
--	3006	C – H stretching
--	2971	CH_2 asym. Stretching
--	2949	CH_2 asymmetric stretching
2170	2880	C – H aliphatic stretching
1592	1669	C = O stretching
1498	1560	Symmetric bend of NH_3^+
--	1514	NH_3^+ bending
--	1439	C-H in plane bending in ring
1330	1324	CH_2 bending
1126	1137	C – C and C=O stretching
1126	1107	C – H in plane bending
1041	1034	C – O stretching of COO^- group
928	892	O – H stretching of carboxylic acid
506	493	Torsional oscillation of NH_3^+

NMR spectral analysis

Proton NMR spectral analysis has also been carried out in order to confirm the structure of the synthesized material. The recorded proton NMR spectrum is shown in **Fig. 3**. The peaks/signals observed at 4.689 and 2.16 ppm are due to the solvent used in the present investigation. The signal at 3.497 ppm is due to the CH_2 group hydrogen with distortion of NH_2 group. Since glycine is the simplest amino acid, there are no other functional group protons are identified in this region.

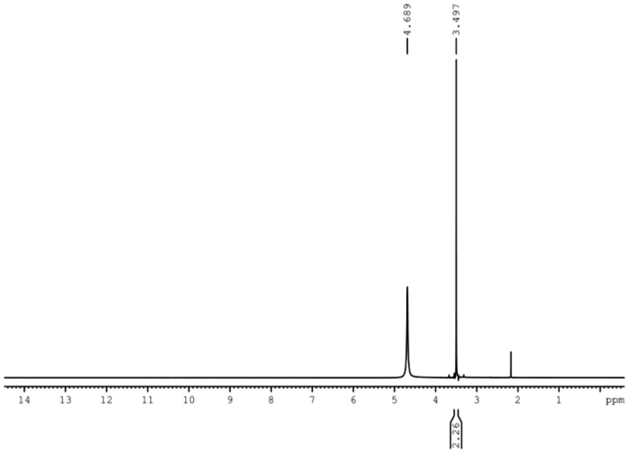

Fig. 3. Proton NMR spectrum of α-glycine grown in the presence of potassium iodide.

Optical Studies

Absorption in the NLO crystal near the fundamental or second harmonic region will lead to loss of conversion efficiency. It is essential to have good transparency in the visible region for a NLO crystal [**4**]. The optical absorption spectrum of the grown crystal has been recorded in the wavelength range of 200–800 nm at room temperature. The recorded UV-Vis absorption spectrum is shown in **Fig. 4(a)**. It is observed that the cut off wavelength is at 250 nm. The crystal has very low absorption starts well below the green region. Hence the grown α-glycine crystal will be useful for the optoelectronic application.

Photoluminescence spectroscopy is a contactless, non-destructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. This excess energy will be dissipated by the sample through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The photoluminescence spectrum was recorded and is shown in **Fig. 4(b)**. The PL measurements were carried out for the excitation wavelength of 275 nm. The emission spectrum was measured in the range 300 – 575 nm. The strong luminescence peak at 418 nm was observed in the emission spectrum. The result indicates that the α-glycine crystals have a strong green emission [**17**].

SHG conversion efficiency measurement has been carried out using Kurtz and Perry technique [**14**].

A Q-switched Nd:YAG laser beam of wavelength 1064 nm with input beam energy of 2.1 mJ/pulse and pulse width 10 ns with a repetition rate of 10 Hz was used. The grown single crystal was powdered with uniform particle size and tightly packed in a micro-capillary tube with uniform bore and exposed to the laser radiation. The bright green light emission (λ = 532 nm) has been observed which indicates the SHG behaviour of the material. The relative SHG efficiency of the α-glycine crystal (38.8 mV) is nearly 1.52 and 0.47 times that of KDP (25.6 mV) and urea (82 mV), respectively.

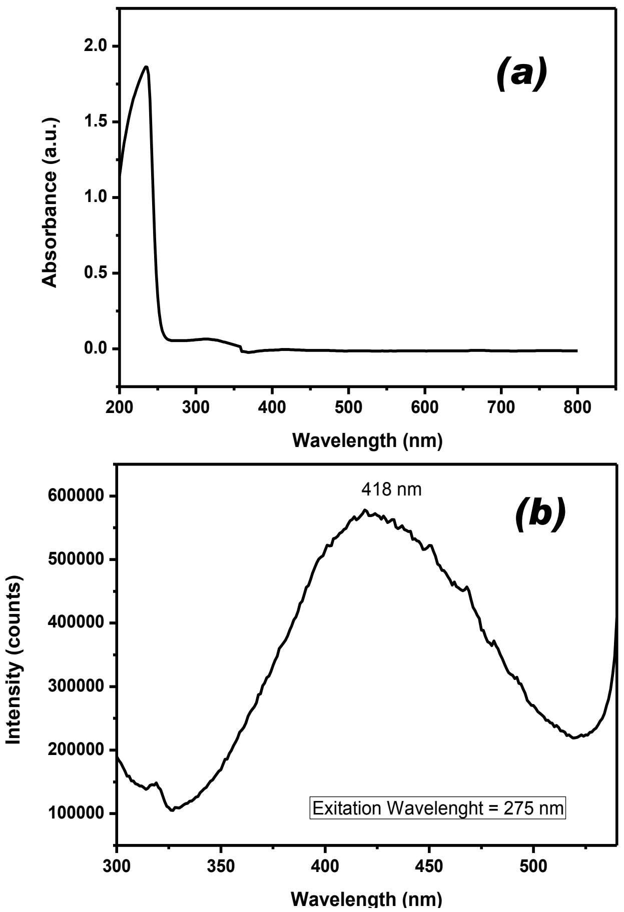

Fig. 4. (a) Absorbtion spectrum and (b) photoluminescence spectrum of α-glycine grown in the presence of potassium iodide.

Thermal analysis

In order to understand the thermal behavior like thermal stability and melting point of the grown crystal, thermal analysis has been performed on the grown crystal powder by obtaining TG/DTA curves as shown in **Fig. 5**. The TG analysis of α-glycine has been carried out between room temperature (28˚C) and 800˚C at a heating rate of 10˚C per min. From the TG curve, it is observed that only two percent of weight has been lost until the temperature reaches 113˚C, which may be due to the loss of physically adsorbed water on the surface of the sample. However, further weight lose upto 8% is observed till 245˚C due to the entire lose of water absorbed into the lattice. From 245 to 280 ˚C another 27% of weight has been decreased due to the decomposition and simultaneous melting of grown crystal which is clearly indicated in the DTA curve by an endothermic peak started at 228˚C and it reaches the peak value at 269.21˚C. During the decomposition it is observed that meager amount of potassium iodide (KI) has been incorporated in to crystal lattice and hence, at the temperature around 280˚C, the KI has exploded due to which the abnormal fluctuation in the weight loss has been observed. Beyond this temperature, the further stages of decomposition of the samples have occurred as observed exothermic transition in the DTA curve.

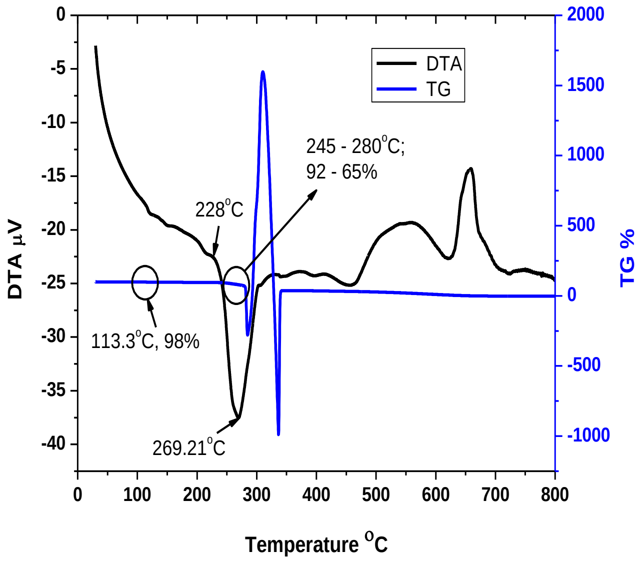

Fig. 5. TG/DTA Curves of α-glycine grown in the presence of potassium iodide.

Dielectric studies

The dielectric constant and the dielectric loss were determined as a function of temperature with frequency. For dielectric measurements, a good quality grown crystal of 3 mm thickness was placed between the electrodes on either side with graphite coating to make it behave like a parallel plate capacitor. The capacitance (C_P) and dielectric loss (tan d) were measured using the conventional parallel plate capacitor method with different frequencies from 1 KHz to 10 KHz at temperature ranges using the Agilent 4284A LCR meter.

The observations were made while cooling the sample. The dielectric constant of the crystal was calculated using the relation

$$\varepsilon_r = \frac{C_p\, d}{\varepsilon_0 A}$$

where, ε_r-dielectric constant, ε_o - dielectric permittivity of free space, C_P - capacitance of crystal, d - thickness, A- area of the crystal [**18**]. **Fig. 6 (a)** and **6 (b)** show the variation of dielectric constant with temperature and variation dielectric loss with temperature, respectively. It is found that the dielectric constant and the dielectric loss generally increased with increase in temperature at lower frequency. The high value of dielectric constant in the low frequency region may be due to the contributions from all four polarizations, namely, electronic, ionic, orientation and space charge polarization [**18**]. The space charge polarization is generally active at low frequencies and high temperature. The low value of dielectric loss at high frequency implies that the crystal possesses good optical quality with lesser defects and this parameter is of vital importance for NLO materials in their applications.

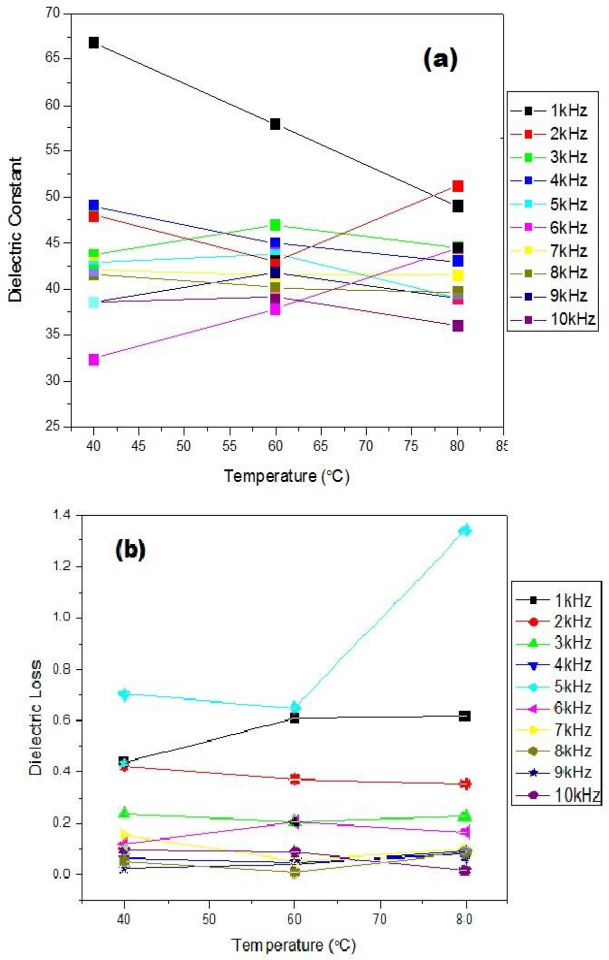

Fig. 6. Variation of (a) dielectric constant and (b) dielectric loss with resspect to frequency and temperature.

Conclusion

Organic NLO material α-glycine was successfully grown as single crystals from the mixture of equimolar potassium iodide with glycine in de-ionized water by slow evaporation technique. The crystal system and crystalline nature of the synthesized material was analyzed by single crystal and powder XRD study, respectively. The presence of various functional groups of the grown crystal was confirmed by FTIR, FT-Raman and NMR spectral analysis. UV-visible spectrum of the grown crystal shows low absorbance with cut-off wavelength at 250 nm. Green emission was observed by photoluminescence spectrum. The SHG relative efficiency of the material was found to be 1.52 times higher than that of standard KDP and comparable to urea. Thermal stability of the grown crystal was studied by TG & DTA analysis and melting point of the material is around 270°C. Thus the characterization confirms the suitability of the grown crystal for NLO applications.

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Author’s contributions

Conceived the plan: PA,PD,RR; Performed the expeirments: PD,MM; Data analysis: PD,PA, PS; Wrote the paper: PD, PA. Authors have no competing financial interests.

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