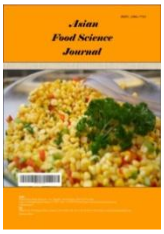

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Structure-Property Relation in Varieties of Millets Grown in Karnataka

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Authors' contributions

This work was carried out in collaboration among all the authors. Author RS designed the study and performed the statistical analysis of XRD data. Author VS wrote the protocol and corrected the first draft of the manuscript. Author NSK carried out SEM, wrote the draft of the manuscript and managed the literature search. Author MSS and PK collected the samples and carried out AC magnetic susceptibility. All authors read and approved the final manuscript.

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ABSTRACT

Aim: This study aims to establish structure-property relation of the varieties of millets grown in Karnataka.
Study Design: Seven different varieties of millets were collected from the farms in Chitradurga district from the state of Karnataka in India.
Place and Duration of Study: This study was conducted between January and April 2020 at the Vijnana Bhavan, University with Potential for excellence, University of Mysore, Karnataka
Methodology: Magnetic property and characterization for seven out of the nine varieties of millets grown in Chitradurga, Hiriyur and Khandenahalli of Karnataka were carried out using X-ray

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diffraction studies (XRD), Energy Dispersive X-ray analysis (EDAX), Raman spectroscopy, SEM and Xplore AC magnetic techniques to understand the physical properties of these samples and to find out the structure-property relation in these millets.

Results: The Foxtail millet is unique in terms of crystallites size, elemental distribution and magnetic properties. The structure-property relation of all the millets is determined.

Conclusion: It is evident from these studies that all the millets are diamagnetic in nature, crystalline like order is less and the major component in all these millets is cellulose. Also the Foxtail millet has excellent structure-property relation.

Keywords: Millets; magnetic susceptibility; crystallite size; Raman shift; FTIR.

1. INTRODUCTION

Millet is a generic term that refers to several small-seeded cereal crop species. In India, millets play a very important role as food and widely cultivated in south India. These are resistant to pests and diseases and their growing time is very short [1,2,3]. There are *Panicum, Echinochloa, Pennisetum* and *Paspalum*. The important millets are Foxtail millet (*Setariaitalica*), Pearl or cat-tail millet (*Penssisetumglaucum*), Proso (*Panicummiliaceum*), Japanese barnyard millet (*Echinocholacrusgalli*), Finger millet (*Eleusinecoracana*), Browntop millet (*Panicumramossum*), Kodo or ditch millet (*Paspalumscrobiculatum*) and Teff millet (*Eragrostistef*) and most of them are grown in India [4]. Various physical properties of these millets have been reported by earlier investigators like the effect of germination on phytase activities [5]. Foxtail millet flour is structurally more stable and resistant to gelatinization and little millet flour is less stable [6]. Dependence of thermal properties and bulk density of millets with moisture [7,8,9]. Hydration kinetics of little millet and proso millet grains and effect of soaking temperature showed positive result [10]. The physical properties of millet, like those of other grains and seeds are essential for design of equipments used for their handling, storing and processing [11,12]. Therefore study on magnetic measurements and characterization of these millets and structure property relation are required.

2. MATERIALS AND METHODS

Seven out of Navadhanya (nine millets) were studied namely Proso, Little, Pearl, Foxtail, Kodo, Barnyard and Brown-top millet. These millets are grown in red and black soil and are collected from farmers of South Indian states. This region receives a moderate rain fall and provides a good climatic condition for cultivation of millets. Here, crops are mainly dependent on rains and underground water. The grains with straw, obtained after three months of harvest, are dried in sunlight. Removal of straw is done by threshing and followed by cleaning, de-stoning and winnowing. Most of these samples are obtained from Chitradurga, Hiriyur and Khandenahalli, Karnataka and are stored in gunny bags after the harvest and the grains are then preserved in air-tight containers. The grains were then grounded finely and sieved through a mesh of pore size 1mm. Images of all the samples are shown in Fig. 1.

2.1 XRD, EDAX, Raman Shift, SEM and AC Magnetic Recordings

XRD recordings of all seven samples were obtained in the range five to sixty degrees (two-theta) with the specifications 30kV and 30mA with a scanning speed of five degrees per minute and a step size of two degrees. All the recordings are shown in Fig. 2.

Table 2 shows the weight percentage of elements present in these millets and quantity of elements within an accuracy of two percent recorded using EDAX equipment.

Natural materials exhibited weak magnetic properties and the AC magnetic susceptibilities of these millets were recorded using a very sensitive instrument XPLORE, Precision quasar technical, New Delhi, India. The variation of chi(prime) and chi(double prime) with frequency were reproduced in Fig. 4 at room temperature 30°C [13]. Any material kept in varying magnetic field will have frequency dependent induced magnetization and this is mainly due to spin magnetic moment of outer most electrons of any element. In materials with permanent magnetic moment, we observe paramagnetic behavior and in the absence of permanent magnetic moment, we observe diamagnetic behavior. The study showed that millets do not have permanent magnetic moment, which was expected since major constituents are normally carbon, oxygen, hydrogen and nitrogen.

(1) (2) (3) (4) (5) (6) (7)

Fig. 1. Sample images of all seven millets: 1-barnyard, 2-browntop, 3-foxtail, 4-kodo, 5-little, 6-pearl and 7-proso

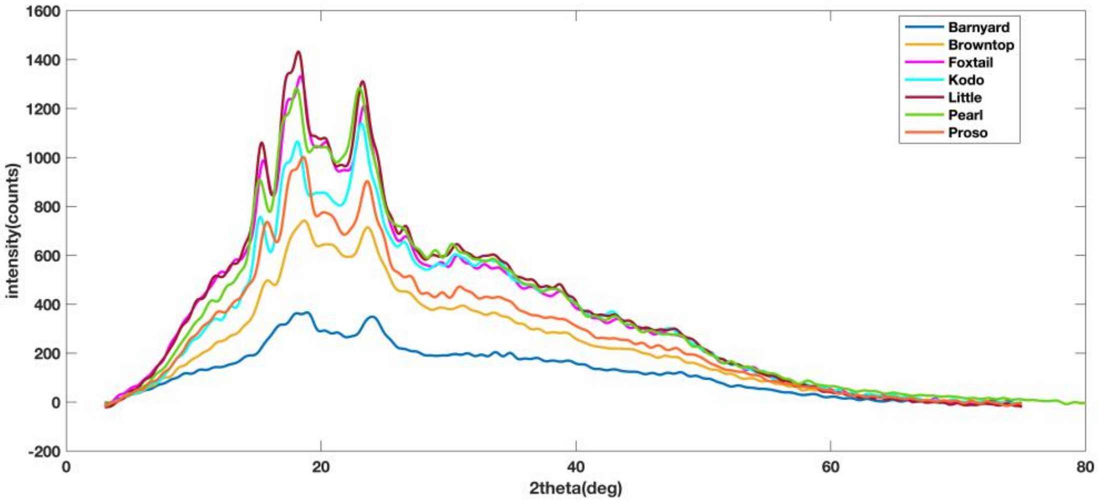
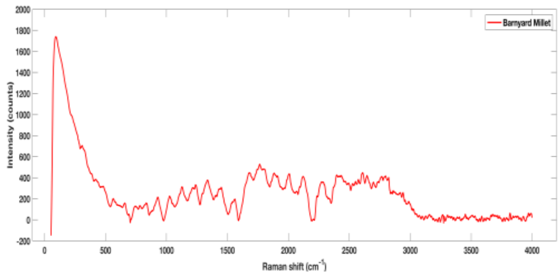


Fig. 2. XRD recordings of all seven millets: 1-barnyard, 2-browntop, 3-foxtail, 4-kodo, 5-little, 6-pearl and 7-proso



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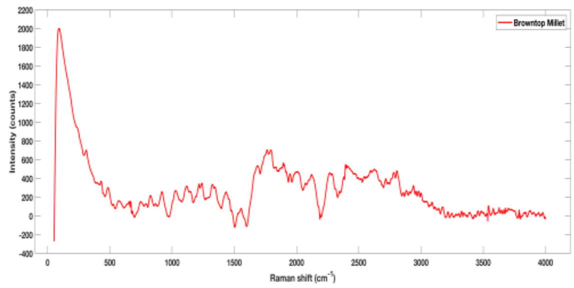

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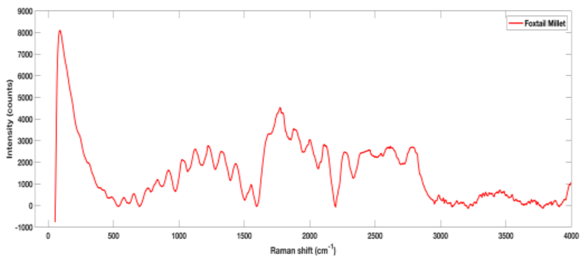

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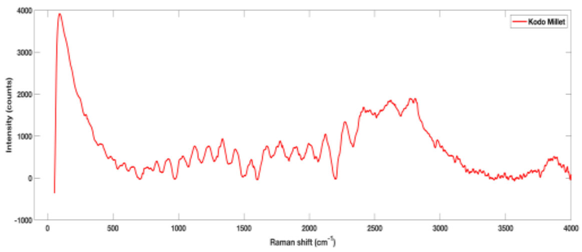

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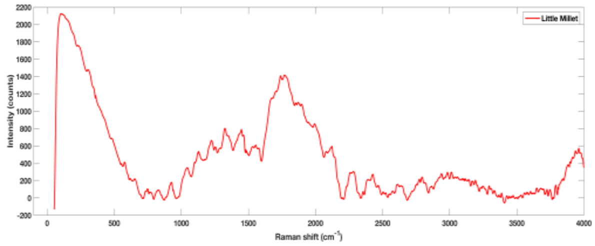

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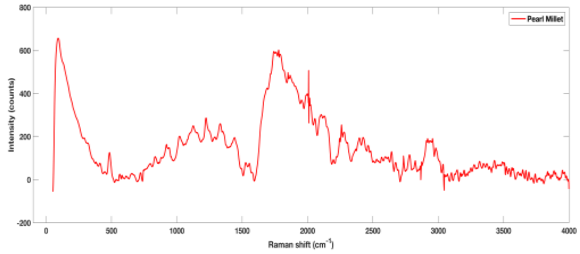

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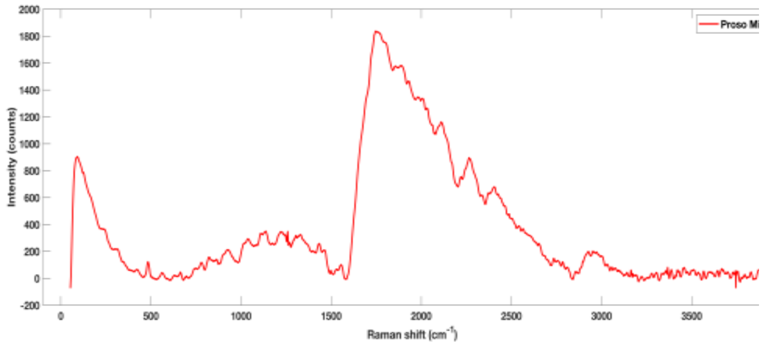

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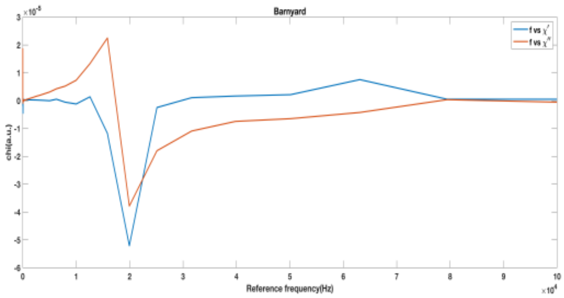
Fig. 3. Raman Shift in millets: 1-Barnyard, 2-Browntop, 3-Foxtail, 4-Kodo, 5-Little, 6-Pearl, 7-Proso



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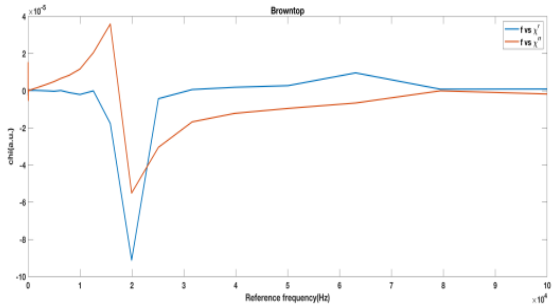

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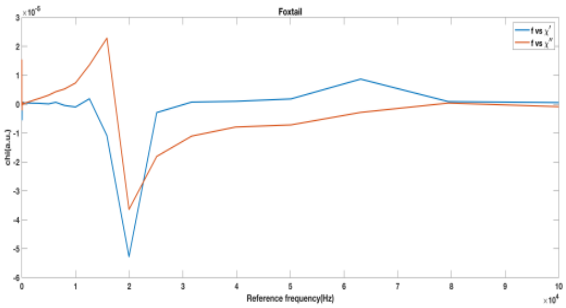

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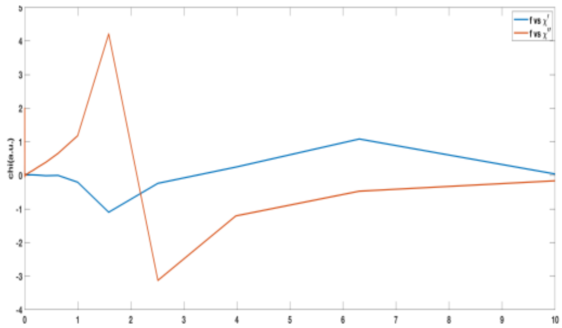

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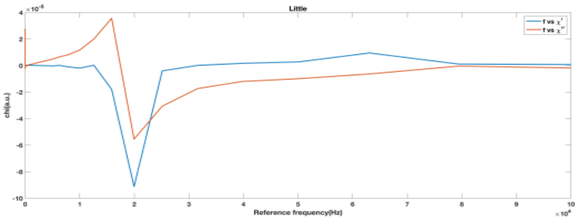

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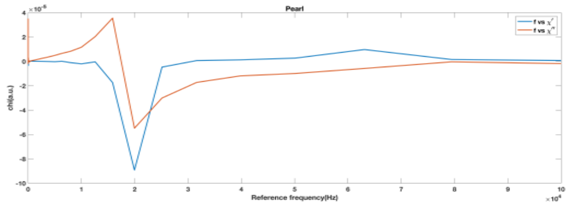

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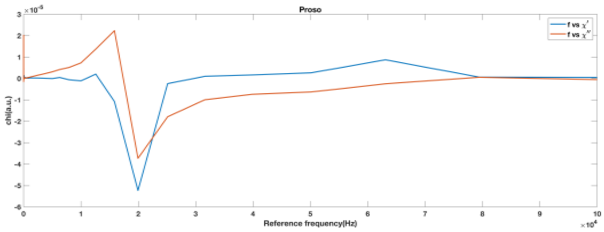

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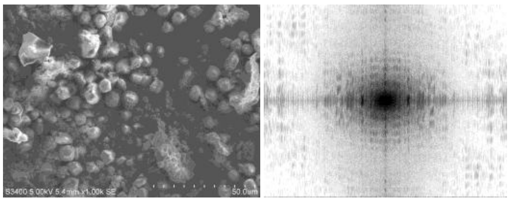
Fig. 4. AC magnetic recording of seven millets: 1-Barnyard, 2-Browntop, 3-Foxtail, 4-Kodo, 5-Little, 6-Pearl, 7-Proso



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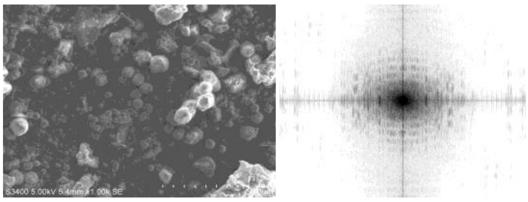

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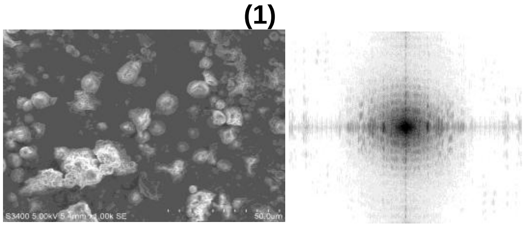

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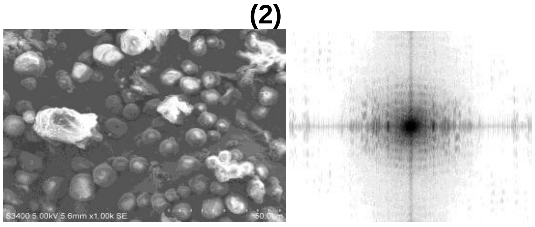

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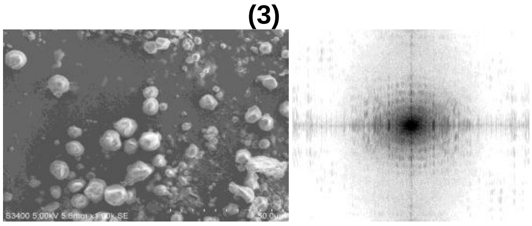

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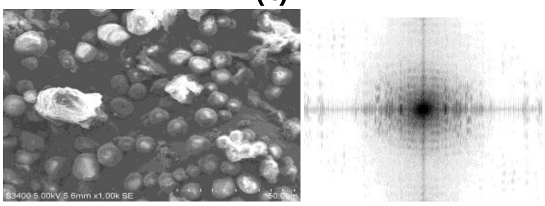

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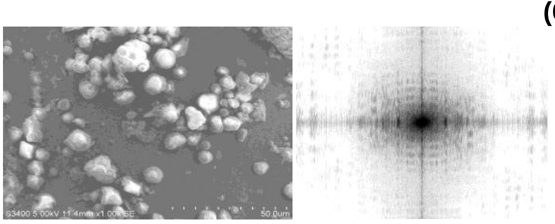

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Fig. 5. SEM photographs and the Fourier Transform of seven millets: 1-Barnyard, 2-Browntop, 3-Foxtail, 4-Kodo, 5-Little, 6-Pearl, 7-Proso

3. RESULTS AND DISCUSSION

Using PeakFit software (https:// systatsoftware .com/downloads/download-peakfit/) the overlapping reflections in XRD recordings were separated. Full width at half maxima (FWHM) was also computed in this software and using Williamson-Hall plot method [13] estimation of crystallite size and strain present in these millets were carried out. Using the positions of Bragg reflections the cell parameters was estimated by trial and error method [14]. The results were documented in Table 1. It was observed that the unit cell volume is maximum in the case of Pearl millet and minimum in Barnyard. Further, the crystallite size is maximum in Foxtail millet and minimum in Proso millet. There is a distinction between these two aspects. Unit cell volume is the primitive cell which encloses the basic chains of molecules, normally four in the case of cellulose, and by symmetry operations reproduces the whole millet sample. Whereas the crystallite size is the average number of Bragg planes times the inter-planar distance 'd' which essentially speaks of the number of such Bragg planes participating in the diffraction process. More the crystallite size value implies the more crystalline like order in the millet.
Elemental analysis indicated the presence of Carbon, Nitrogen, Oxygen, Magnesium, Phosphorous and Potassium as shown in Table 2.

Raman Shift and their functional group in these millets are tabulated in Table 3.

It is observed that Raman Shift accounts for the presence of acoustic and longitudinal lattice vibrational modes of alicyclic, aliphatic chain, C=C bonding in all the seven millets. The Browntop, Kodo and Pearl millets show the presence of C-H Bond. These are similar in nature when compared to cellulose.SEM images for all the millet samples along with Fast Fourier transforms in Fig. 5 show fine ordering at the magnification of 50 microns. This ordering is same in all seven millets as can be seen from FFT photos. The AC magnetic susceptibility of χ' and χ'' of all millets show that there is a maximum component around 20kHz. The values of χ' and χ'' vary from sample to sample and these measurements indicate that all seven millets are diamagnetic in nature. Order of magnitude remains same in all the seven millets within the experimental errors (see Table 4).

3.1 Establishing the Correlation between Structure and Property in Millets Studied

For this purpose two physical parameters 1) crystallite size and 2) χ', real part of magnetic susceptibility) were compared. In statistics, there is a standard functional analysis technique. For brevity, the equation used was reproduced for this purpose based on previous study [15]. Any physical parameter theta behaves as a function of t for the i^{th} sample and was given by

$$q_i(t) = m_i(t) + SA_{ik}q_k(t) \quad (1)$$

Where the infinite sums has been truncated to finite constant K. The procedure is technically involved and we refer the interested reader to [15]. In the above equation, q refers to measured physical parameter like crystallite size and real part of magnetic susceptibility and t refers to different samples and it is numbered as 1-7 for computation purpose. We have carried out computation using FPCA package (written in MATLAB: The MathWorks Inc., Natick, MA, USA available at http:// www. stat.ucdavis.edu/PACE/). The following figures reflect the correlation between structure and parameters.

Table 1. Crystalline parameters of seven millets using XRD

Cell parameters	a in Å	B in Å	c in Å	α	β	Γ	Cell volume (Å)^3	Crystallite size in Å	Strain in %
Barnyard	11.3	5.3	9.6	90	91.8	90	584.2	19.7	2.7
Browntop	20.3	18.0	3.8	90	90	90	1393.4	15.8	3.6
Foxtail	11.8	11.3	8.2	90	90	90	1107.1	28.9	1.9
Kodo	15.1	15.5	5.3	90	123.6	90	1038.5	13.9	7.1
Little	11.6	8.7	7.7	90	90	90	784.1	18.9	3.2
Pearl	14.7	12.4	9.5	90	90	90	1738.7	19.8	4.7
Proso	12.1	9.5	11.2	90	99.4	90	1278.7	12.7	6.6

Table 2. EDAX results of element percentage in millets

Elements	Carbon	Nitrogen	Oxygen	Magnesium	Phosphorous	Potassium
Barnyard	60.8	---	37.84	0.32	0.62	0.42
Browntop	60.51	---	39.19	0.12	0.17	---
Foxtail	61.61	---	37.23	0.41	0.48	0.28
Kodo	58.04	---	41.53	---	0.43	---
Little	29.37	34.46	35.66	0.20	0.21	0.08
Pearl	55.30	---	44.55	---	---	0.15
Proso	57.34	---	41.44	0.46	0.56	0.19

Table 3. Raman shift in seven millets

Sl. no	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
Barnyard	113.95 cm^{-1} Lattice Vibrations LA mode	328.03 cm^{-1}	1771.80 cm^{-1} c=c (strong)	-	2578.19 cm^{-1} S-H (strong)
Browntop	106.10 cm^{-1} Lattice Vibrations LA mode (strong)	1226.77 cm^{-1} C-C alicyclic, aliphatic chain	1775.50 cm^{-1} C=C (strong)	2937.61 cm^{-1} C-H (strong)	-
Foxtail	120.80 cm^{-1} Lattice Vibrations LA mode (strong)	1194.94 cm^{-1} C-C alicyclic, aliphatic chain	1865.99 cm^{-1} C=C (strong)	-	2584.56 cm^{-1} S-N (strong)
Kodo	124.55 cm^{-1} Lattice Vibrations LA mode (strong)	1126.33 cm^{-1} C-C alicyclic, aliphatic chain	1808.99 cm^{-1} C=C (strong)	2801.39 cm^{-1} C-H (strong)	2589.67 cm^{-1} S-H (strong)
Little	135.97 cm^{-1} Lattice Vibrations LA mode (strong)	1293.31 cm^{-1} C-C alicyclic, aliphatic chain	1767.31 cm^{-1} C=C (strong)	-	-
Pearl	121.47 cm^{-1} Lattice Vibrations LA mode (strong)	191.74 cm^{-1} C-C alicyclic, aliphatic chain	1758.99 cm^{-1} C=C (strong)	2940.19 cm^{-1} C-H (strong)	-
Proso	122.65 cm^{-1} Lattice Vibrations LA mode (strong)	-	1777.46 cm^{-1} C=C (strong)	-	-

Table 4. AC magnetic results of seven millets

Sample	χ' x10^{-5}	χ'' x 10^{-5}
Barnyard	-5.21	-3.79
Brown	-9.11	-5.50
Foxtail	-5.27	-3.61
kodo	-1.09	-4.21
Little	-9.11	-5.53
Pearl	-8.89	-5.48
Proso	-5.23	-3.72

From the functional analysis, there are three aspects which emerge clearly. Firstly there is a correlation between crystallite size and real part of magnetic susceptibility with seven millets. If there were 'no' correlation then the number of principal components would have reduced to zero and the three dimensional correlation surface shown in Figs. (A) and (D) cannot be computed. This is the test for the correlation to exist. Secondly, the mean values are computed on the basis of correlation between physical parameters of seven millets and among millets Foxtail and Kodo millets show a maximum of crystallite size and real part of magnetic susceptibility. Further, A plot of unit cell volume and crystallite size and magnetic measurement indicate significant variation which can be fitted with a linear function.

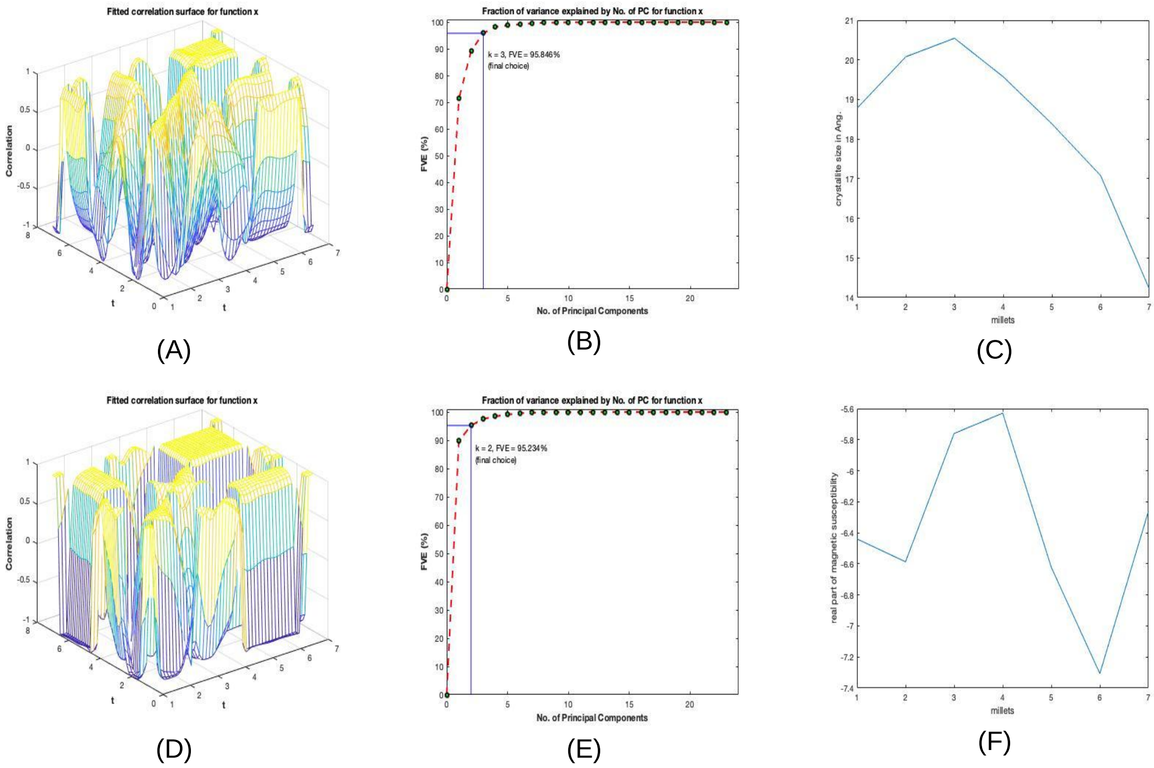

Fig. 6. Functional analysis of crystallite size and real part of magnetic susceptibility with seven samples (indicated in figure 't=1-7') :(A) Correlation surface of crystallite size with seven millets; (B) number of principal components of crystallite size with seven millets and (C) computed mean value of crystallite size with seven millets. Similarly (D), (E) and (F) refers to correlation, number of principal components and mean value of real part of magnetic susceptibility with seven millets

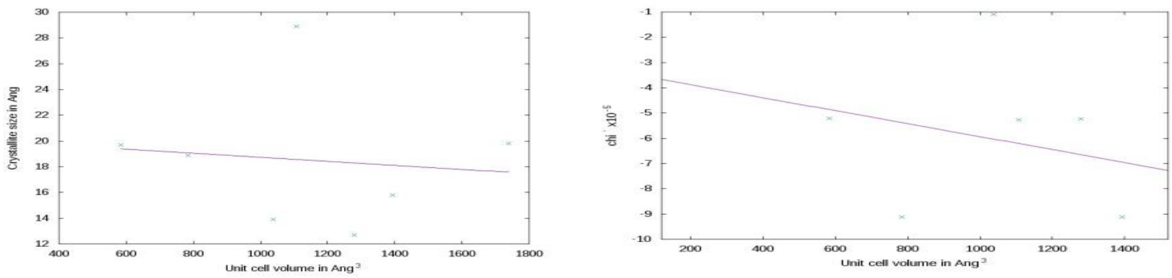

Fig. 7. Least square fit for crystallite size and real part of magnetic susceptibility with unit cell volume for seven millets

Fig. 7 indicates that there is a trend of increasing physical parameters value with increase in unit cell volume. Further, maximum unit cell volume is observed for Pearl millet and minimum for Barnyard millet.

4. CONCLUSION

The characterization of seven different varieties of millets cultivated in south India which are different from each other in various physical parameters with a motivation to establish structure-property relation is carried out. The following conclusions emerge from this study:

The XRD analysis indicates that crystalline like order is less since crystallite size is of the order of 20Å. Normally in any crystal this size is of the order of 200Å. Essentially, a few Bragg planes participate in diffraction process. Raman shift analysis identifies that the major component in all these millets is cellulose. FFT's of SEM images indicate variation of ordering in different millets. There are no sharp reflections in the FFT image.

AC magnetic susceptibility accounts for the diamagnetic behavior in these millets. Correlation between crystallite size and millets and also that between magnetic properties with millets is very well established using Functional analysis of the data. From this study it is evident that Foxtail millet has unique value of crystallites size, elemental distribution and magnetic properties.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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