Original Research Article

Structure-property relation in varieties of millets grown in Karnataka

ABSTRACT

Aim: This study aims to establish structure-property relation of the 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 – April 2020 at the Vijnana Bhavan, University with Potential for excellence, University of Mysore, Karnataka
Methodology: Magnetic property and cCharacterisation forof seven out of the nine different varieties of millets grown in Chitradurga, Hiriyur and Khandenahalli of Karnataka wereare carried out. usingUsing X-ray 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 structure-property relation is determined using Stochastic process and the data reported here.
Conclusion: We do observe from these studies that Foxtail and Kodo millets have excellent structure-property relation.

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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][3][4]. There are *Panicum, Echinochloa, Pennisetum* and *Paspalum*. The important millets are Foxtail millet (*Setaria italica*), Pearl or cat-tail millet (*Penssisetum glaucum*), Proso (*Panicum miliaceum*), Japanese barnyard millet (*Echinochola crusgalli*), Finger millet (*Eleusine coracana*), Browntop millet (*Panicum ramossum*), Kodo or ditch millet (*Paspalum scrobiculatum*) and Teff millet (*Eragrostis tef*) and most of them are grown in India [5]. Therefore study on nmgnetic measurements and characterisation of these millets and structure property relation are required. Various physical properties of these millets have been reported by earlier investigators [8][12][14][15]. Hydration kinetics of little millet and proso millet grains and effect of soaking temperature were reported by Balasubramanian and Visvanathan [7]. 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 [9][13].

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2. MATERIAL AND METHODS

Seven out of Navadhanya (nine millets) were~~are~~ studied~~. They are~~ 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 ~~S~~straw ~~is removed~~ ~~b~~by threshing and~~ this is~~ 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 Figure-1.

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

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 a~~re~~s shown in Figure 2.

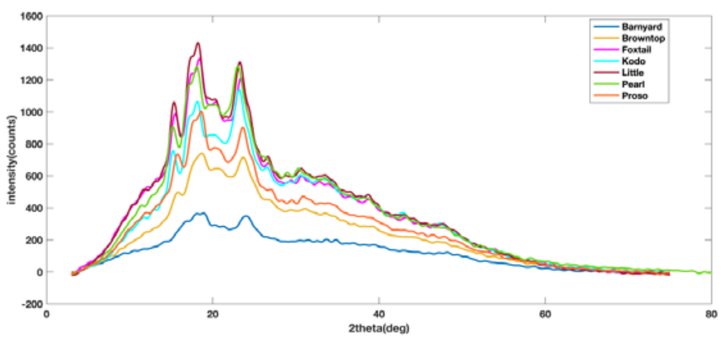
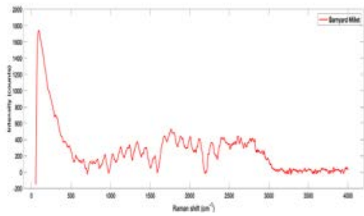


Figure 2: XRD recordings of all seven millets: 1-barnyard, 2-browntop, 3-foxtail, 4-kodo, 5-little, 6-pearl and 7-proso.

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



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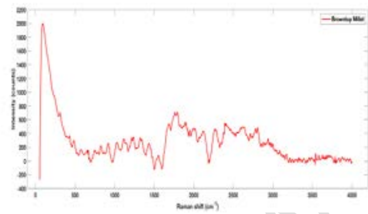

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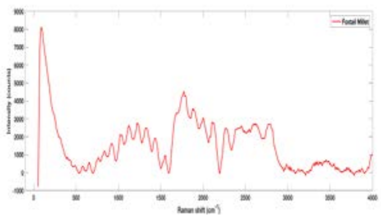

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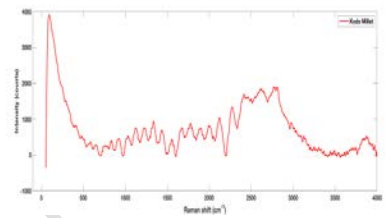

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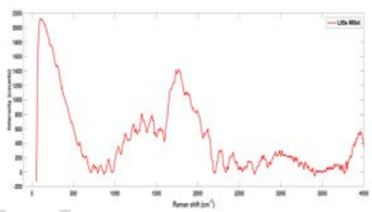

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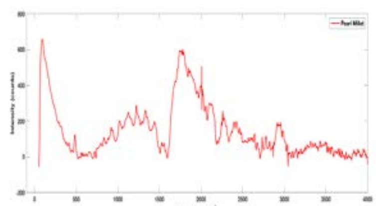

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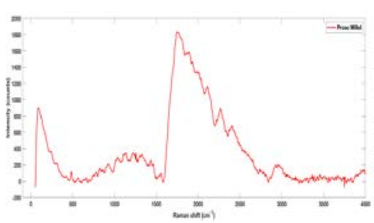

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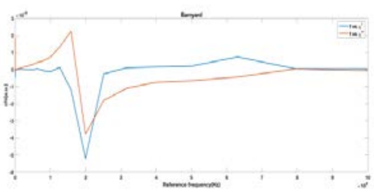
Figure 3: Raman Shift in millets: 1-Barnyard, 2-Browntop, 3-Foxtail, 4-Kodo, 5-Little, 6-Pearl, 7-Proso.

Natural materials exhibited weak magnetic properties and the AC magnetic susceptibilities of these millets weare recorded using a very sensitive instrument XPLORE, Precision quasar technical, New Delhi, India. The variation of chi (prime) and chi (double prime) with frequency weare reproduced in Figure 4 at room temperature of 30˚C [2]. Any material kept in varying magnetic field will have frequency dependent induced magnetisation 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 behaviour and in the absence of permanent magnetic moment, we observe diamagnetic behaviour. The Our studyies showed that all millets do not have permanent magnetic moment whichmoment, which wais expected since major constituents are normally carbon, oxygen, hydrogen and nitrogen.



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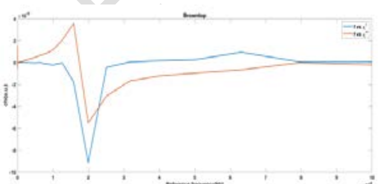

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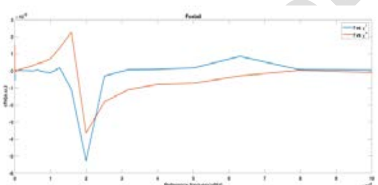

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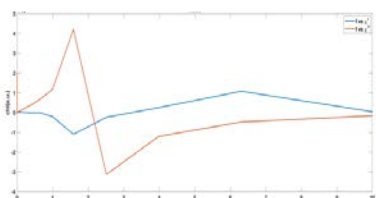

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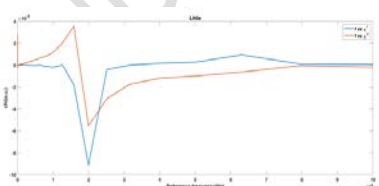

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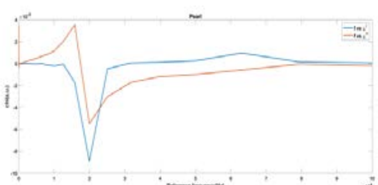

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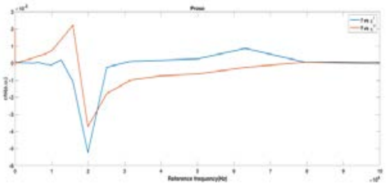

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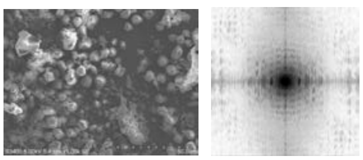
Figure 4: AC magnetic recording of seven millets: 1-Barnyard, 2-Browntop, 3-Foxtail, 4-Kodo, 5-Little, 6-Pearl, 7-Proso.



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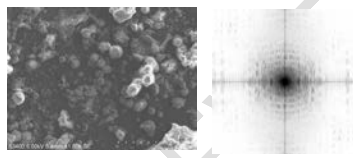

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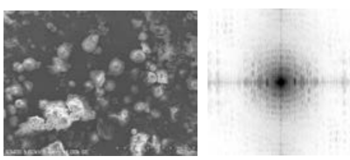

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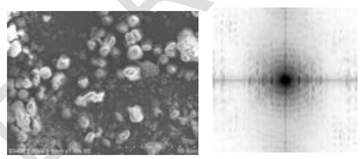

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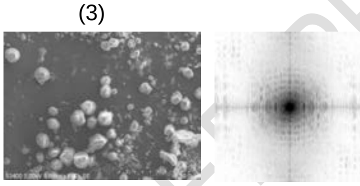

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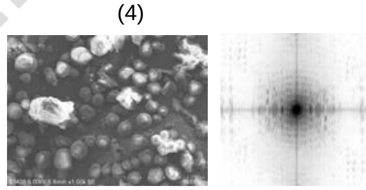

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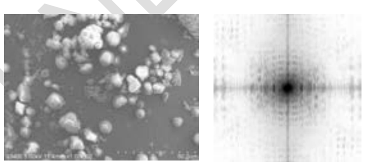

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Figure 5: SEM photographs and the Fourier Transform of seven millets: 1-Barnyard, 2-Browntop, 3-Foxtail, 4-Kodo, 5-Little, 6-Pearl, 7-Proso.

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3. RESULTS AND DISCUSSION

Using PeakFit software (https://systatsoftware.com/downloads/download-peakfit/) the overlapping reflections in XRD recordings were separated. FWHM wa~~i~~s also computed in this software and using Williamson-Hall plot method [2]~~ we have~~ estimation of~~ed~~ crystallite size and strain present in these millets were carried out. ~~Further U~~using the positions of Bragg reflections ~~we have estimated~~ the cell parameters was estimated by trial and error method [17]. The results we~~a~~re documented~~given~~ in Table 1. It wa~~i~~s 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 reproduced 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.

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Table 1: Crystalline parameters of seven millets using XRD

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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

Elemental analysis indicated~~s~~ the presence of Carbon, Nitrogen, Oxygen, Magnesium, Phosphorous and Potassium as~~nd they are given~~ shown in Table 2~~ in percentage~~.

Table 2: EDAX results of element percentage in millets.

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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

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Proso	57.34	---	41.44	0.46	0.56	0.19

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

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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)	-	-

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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 Figure 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).

Table 4: AC magnetic results of seven millets.

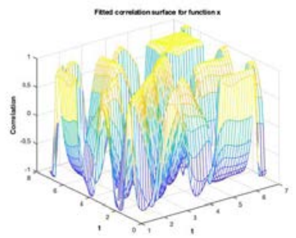
Sample	χ' $\times 10^{-5}$	χ'' $\times 10^{-5}$
Barnyard	-5.21	-3.79
Brown	-9.11	-5.50
Foxtail	-5.27	-3.61
kodo	-1.09	-4.21
Little	-9.11	-5.53
Pearl	-8.89	-5.48
Proso	-5.23	-3.72

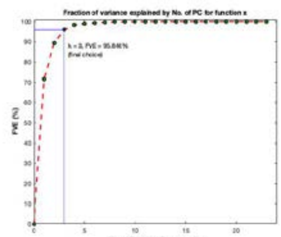
3.1 Establishing the correlation between structure and property in Millets studied:

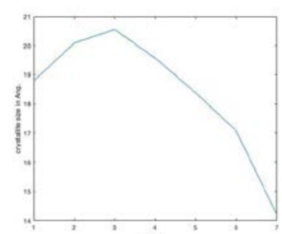
For this purpose we have considered two physical parameters (crystallite size and 2) χ', real part of magnetic susceptibility)namely were compared, 1) crystallite size and 2) χ', real part of magnetic susceptibility. In statistics, there is a standard fFunctional analysis technique which we use here. For brevity, we reproduce the equation used was reproduced for this purpose and for details one can refer to our earlier paper based on previous study [16]. Any physical parameter theta behaves as a function of t for the ith sample and wais given by

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

where the infinite sums has been truncated to finite constant K. The procedure is technically involved and we refer the interested reader to [16]. 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.







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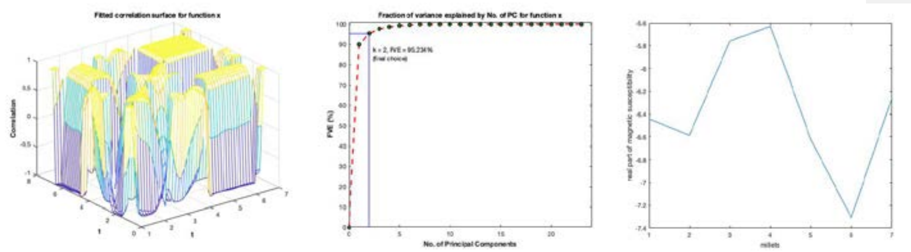
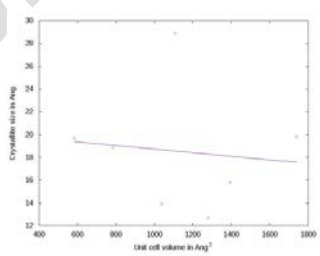


(D) (E) (F)

Figure 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.

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 Figures (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.



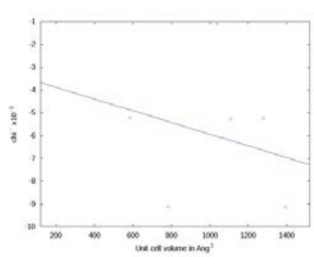


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Figure 7: Least square fit for crystallite size and real part of magnetic susceptibility with unit cell volume for seven millets.

Figure 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

We have characterised 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. The following conclusions emerge from this study:

1. 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.
2. Raman shift analysis identifies that the major component in all these millets is cellulose.
3. FFT's of SEM images indicate variation of ordering in different millets. There are no sharp reflections in the FFT image.
4. AC magnetic susceptibility accounts for the diamagnetic behaviour in these millets.
5. Correlation between crystallite size and millets and also that between magnetic properties with millets is very well established using Functional analysis of the data.
6. From this study it is evident that Foxtail millet has unique value of crystallites size, elemental distribution and magnetic properties.

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