https://doi.org/10.48047/AFJBS.6.12.2024.2026-2033

African Journal of Biological Sciences

Journal homepage: http://www.afjbs.com

Research Paper Open Access

Synthesis, Structural and Fractal analysis of BFO Nanoparticles

Vivek Kumar Bajpai[1], Ajeet Kumar Rai[1] R.R. Awasthi[2*]

[1]Department VIAET, Mechanical Engineering, Shuats, Prayagraj-211007

[2]Faculty of Engineering and Technology, KhwajaMoinuddin Chishti Language University Lucknow, 226013, (U.P.) India

Email:bajpai.vivek4@gmail.com

Article History
Volume 6, Issue 12, 2024
Received: 30 May 2024
Accepted : 30June 2024
Doi:
10.48047/AFJBS.6.12.2024.2026-2033

Abstract

The main objective of the present investigationto examined the impact of annealing temperaturevarying from 450 °C to 500 °C on bismuth ferrite (BFO)thin films prepared by spray pyrolysis method. The X-ray diffraction (XRD)confirmed that BFO havetypical rhombohedralphase with no intermediate impurity phasespresent in the sample.The average crystallite sizes as calculated using Scherer's equation found to be in the range of ~15to 20 nm.The crystallite size and microstrain as calculated from Williamson-Hall methods were found to be ~17.67 nm, 22.35 nm 28.54 nm and 0.028, 0.021 respectively.The atomic force microscopy (AFM)revealedthat BFONPs are formed nanorods shape topography,symmetrically distributed throughout on the surface of the films. The surface roughness increases from ~4.56 nm to 7.68 nm with increase the annealing temperature indicates modified the crystal structure of thin films.Thefractal dimension values was observed and found to be 1.64 and 1.96. It to be seen that, increasing values of the fractal dimension with increasing annealing temperature 450 °C to 500 °C respectively. This result indicates that can be employed to describe the variation of theentire grain morphology along direction of the growth. Also, unlikeRMS roughness, the fractal dimension contains spatial information andprofile deviation information.

Keywords: Multiferroics; fractal dimension; BFO; XRD;AFM

1. Introduction

During the last few decades, multiferroic materials have attractedconsiderable attention, due to their coupling ferroelectric and antiferromagnetic orders in the samephase [1,2]. Consequently discovery of the magnetoelectric (ME) effect has beenconsidered to bepromising for potentialapplications towards developing new kind of functional devices.There are very few energy-efficient single phase multiferroic materials that exist at room temperature [3]. The preparation of single phasenano-structured powders is essential to enhance the ferroelectric and magnetic properties. Multiferroic bismuth ferrite ($BiFeO_3$), which is commonly called as BFO is a popular bismuth-based material, which holds an excellent ferroelectric order and widely used in used in high temperature magnetoelectric coupling devices.Currently, various advanced techniques have been reported to prepare multiferroic materials,which can tailor the surface area

to volume ratio and improve the microstructural and magnetic properties. The popular examples of such techniques are solid state reaction, sol-gel, hydrothermal [4-9] method etc.

BFO's intrinsic issues, such as high leakage, high loss, low polarization, variable oxidation state (+2, +3, +4) of Fe, and associated phases(Bi-rich phases: Bi_2O_3 and $Bi_{25}FeO_{39}$, Fe-rich phases: $Bi_2Fe_4O_9$ and Fe_2O_3) etc. hinder its commercial utilization. Itisalsopredictedthatsubstitutionof Feionswith3dtransition ions likeCr, Mn, Co, Ni and Cu increases the magnetic moments as well as magnetic anisotropies and hence improve the magnetic, optical and ferroelectric properties of BFO nanostructure [10-14]. Some transition elements (Mn, Zn, Ti, Al, etc.) are used to substitute Fe to reduce the large leakage current and improve the surface topography [15]. On the otherhand some metal oxides nanostructures have been extensively used in present scenario but its limited application in functional device [16-18]. In the presentresearch paper we have examined the impact of annealing temperature on bismuth ferrite (BFO) thin films prepared by spray pyrolysis method.

2. Experimental

High purity chemicals used were bismuth nitrate $Bi(NO_3)_3.5H_2O$ (≥99 %, Merck) and iron nitrate $Fe(NO_3)_3.9H_2O$(≥99 %, Merck). These materials were weighedaccurately in suitable stoichiometric amounts. Iron nitrate andbismuth nitrate were dissolved in1:1 molar ratio. The precursor solution was continuously stirred for 2 hours at 70 °C to obtain uniform, transparent precursor solution. The glass substrates were also cleaned with organic solvents methanol and acetone to remove dust particle/contaminant present on the glass surface. Finally, the precursor solutions were sprayed with the help of a nebulizer on the glass substrates at 400 °C for 5 minutes, maintaining solution flow rate of 0.2 ml/min.The as synthesized thin films were annealed using a SiC furnace in an open-air environment for 3 hours at 450 °C to 500 °C in order to obtain appropriate crystallization. The structural and morphological properties of pure BFO nanomaterials were characterized by X-ray diffraction(XRD) using Rigaku ultima IV (CuKα λ ~ 1.5404 Å) and atomic force microscopy (AFM) Nanomagnetic Instrument.

3. Results and discussion

3.1. Structural analysis

Figure 1(a) depicts the XRD pattern of BFOnanostructures. The observed XRD peaks match well with the JCPDS (072-2112) of rhombohedral phase with R-3m space group.There are no intermediate impurity phasesvisible in the XRD pattern of BFO. The average crystallite sizes of BFOthin films annealed at 450 °C to 500 °C were determined using Scherer's equation;

$D = \frac{K\lambda}{\beta \cos\theta}$, where K is constant (K= 0.9), λ is the X-ray wavelength of CuKα used in XRD, θ is the Bragg's angle and $\beta$is the full-width at half-maximum (FWHM). The average crystallite size was calculated using Scherer's equation found to be in the range of ~15.4 nm to 20.7 nm.

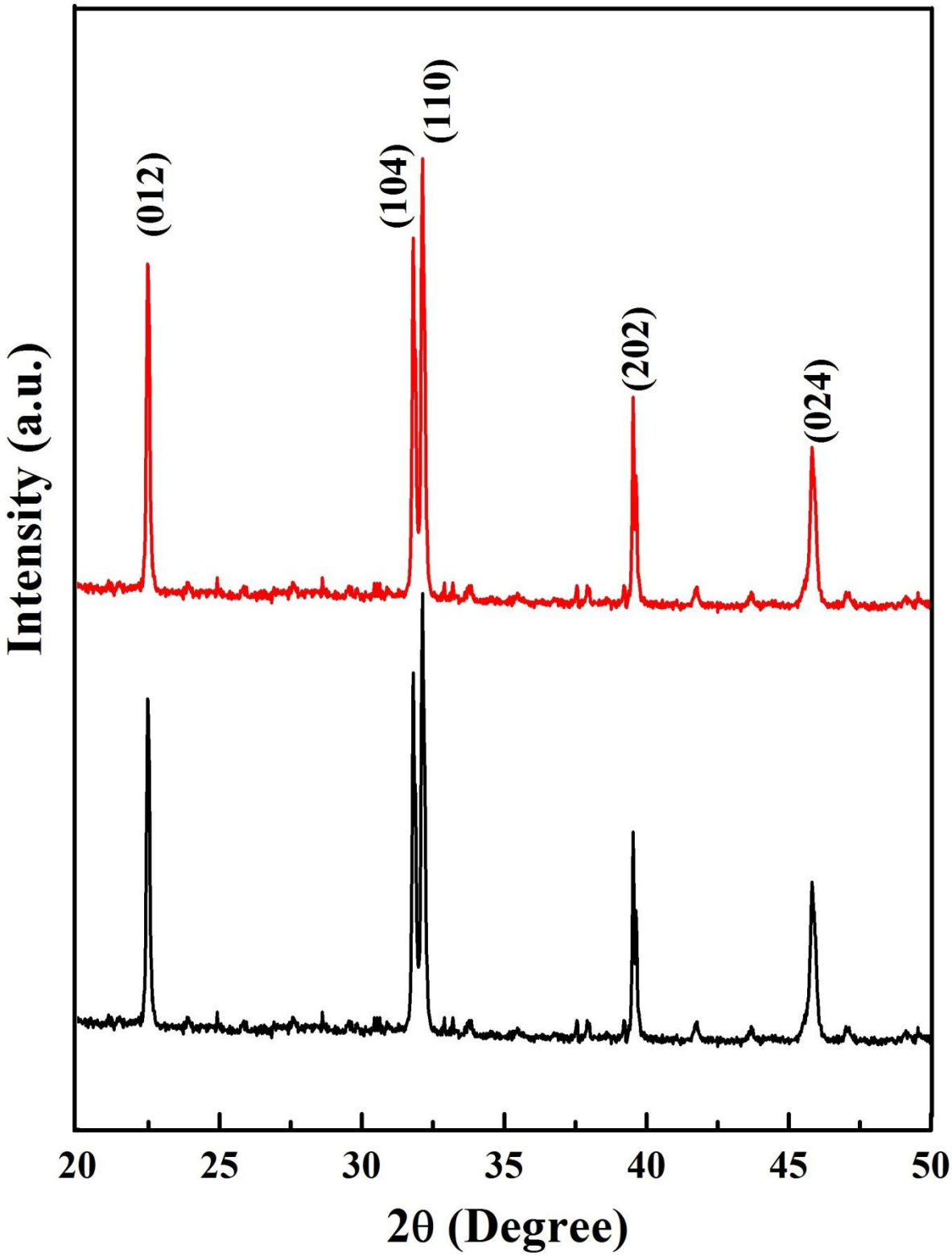

Figure 1 X-ray diffraction patterns of BFO thin films annealed at 450 ^{0}C and 500 ^{0}C.

The micro strain and crystallite size are also calculated fromWilliamson-Hall (W-H) plot with following relation$\beta Cos\theta = \frac{k\lambda}{D} + 4\varepsilon Sin\theta$Figure 2 shows W-H plot of graph plotted against βCosθ versus 4Sinθ, gives the value of lattice strain (ε) and inverse of intercept gives the

value of crystallite size (D) corresponding to zero stain.The crystallite sizeand microstrain as calculated from Williamson-Hall methods were found to be ~17.67 nm, 22.35 nm 28.54 nm and 0.028, 0.021 respectively.

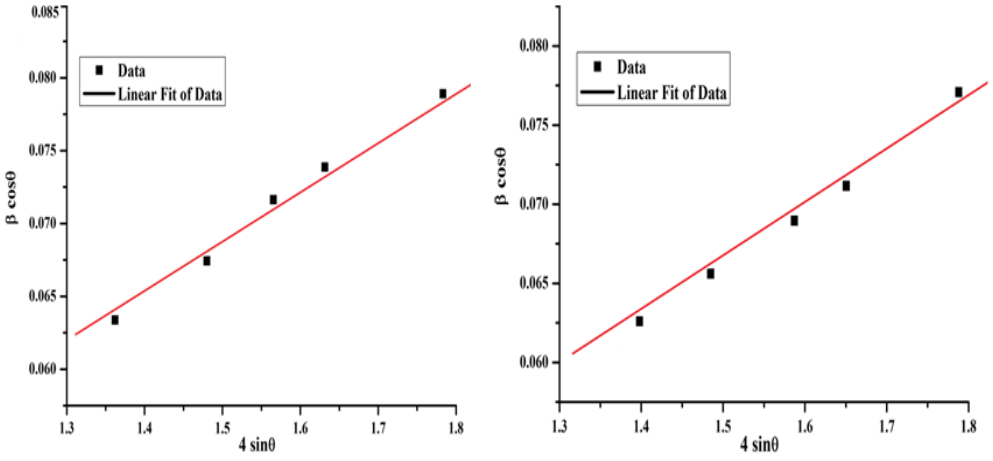

Figure 2(a-b) Williamson-Hall plot of BFO thin films annealed at 450 ^{0}C and 500 ^{0}C.

3.2. Surface topography

3.2.1 Atomic force microscopy (AFM) studies

Figure 2(a)-(b) exhibits the AFM images of BFO thin films prepared by spray pyrolysis techniquecarried out by atomic force microscopy (AFM) technique. It micrograph reveals that the formation of nanorods shape topography with granular growth of BFO thin films. The nanorods shape topography of BFO thin films distributed throughout the sample surface with clear grain and grain boundaries. Furthermore increase the annealing temperature the density and growth of nanorods shape topography of the film increases as shown in figure 2(a-b). The particle sizes as estimated from AFM image ofBFO sample annealed at 450 °C and 500 °C were found to be about ~150 nm and ~200 nm respectively. Thus, increases the particles size with increasing of annealing temperature are well consistent with the obtained from the X-RDmeasurements. The surface parameters, such as root mean square (RMS) surface roughnessof BFO thin filmsannealed at 450 °C and 500 °C were calculated and found to be ~4.56 nm to 7.68 nm respectively. This increase in roughness with increasing annealing temperatureis indicating the enhancement of surfaces defectin of the BFO thin films.

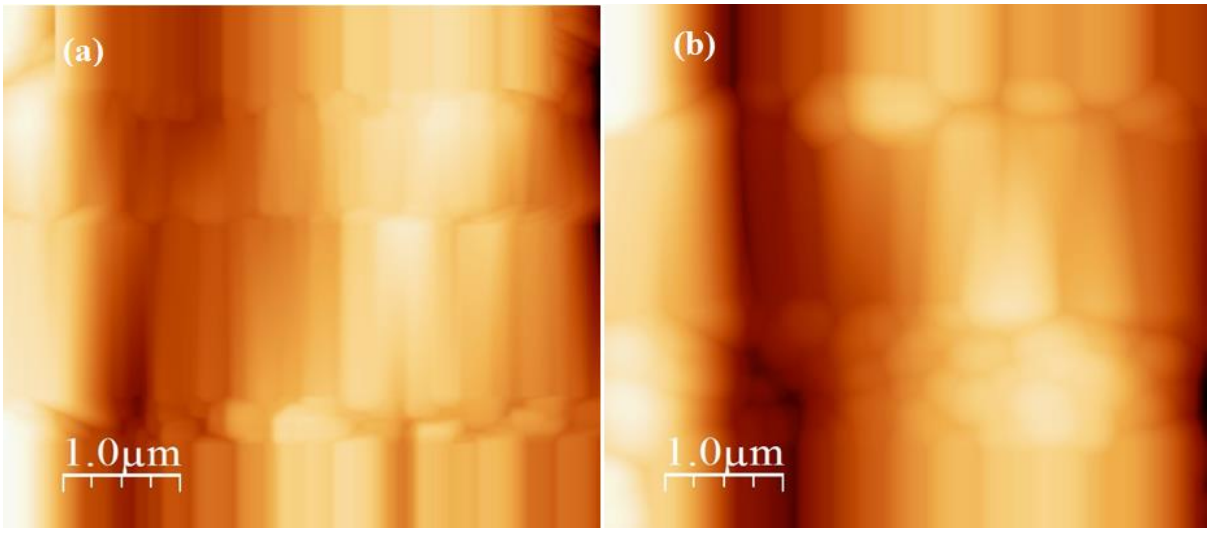

Figure 2(a-b) 2-D AFM surface topography of BFO thin films annealed at 450 ^{0}C and 500 ^{0}C. Figure 2(c)-(d) exhibited the high resolution contour plot of AFM images, which demonstrate thatBFO thin films have symmetric growth of grains in-plane shapes with elliptical bases. Furthermore increases the annealing at 450 °C to 500 °C BFO thin film contour plot clearly revealed thatenhance the symmetric growth and increase the in-plane shapes with elliptical bases.

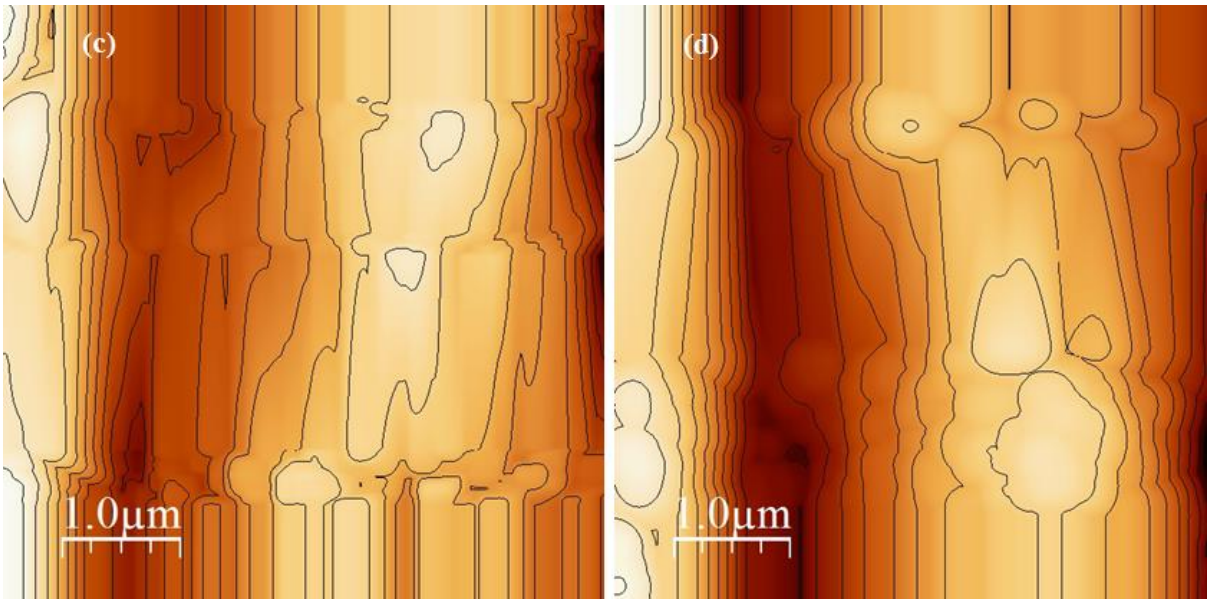

Figure 2(c-d) Contour plot of BFO thin films annealed at 450 ^{0}C and 500 ^{0}C.

Fig. 2(e) & 2(f) exhibit the 3-D AFM images, which demonstrate that BFO NPs have uniform grains of nanorods distribution with average height of 716.7 nm and 726.1 nm. The modification and small increment of Z-height distribution may be caused due to creates of lattice strain. Hence, it can be used fractal analysis to analysis of the grain distributionquantitatively and gives information about the random distribution of the grain.

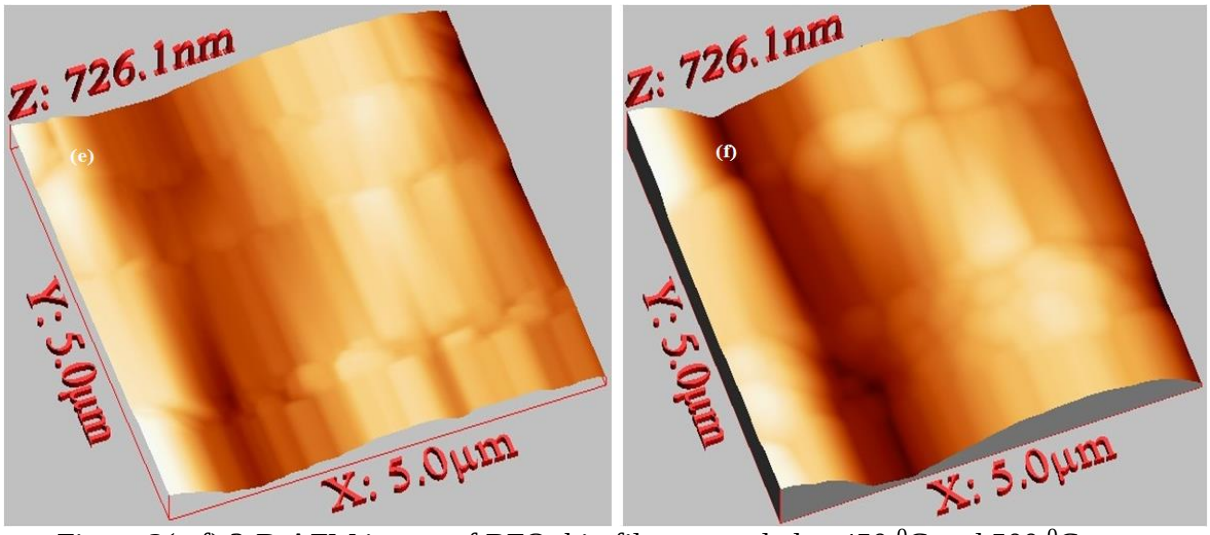

Figure 2(e-f) 3-D AFM image of BFO thin films annealed at 450 ^{0}C and 500 ^{0}C.

3.2.2 Fractal Analysis

Figure 3(a) & 3(b) exhibit fractal analyses of BFO materials using Power spectral density (PSD) methodwith increasing annealing temperature from 450 °C to 500 °C of BFO sample. The advantages of the fractal approach are the possibility ofconsidering the complex fracture morphology of the surfaces. The fractal dimension isa possible measure of degree of surface roughness and depends onspatial distribution of grain within the thin film, crystal size and thecombined effects of morphology. Power spectral density (PSD) method can beemployed to calculate fractal dimension. In this method, fractal dimension (*D*) ranging from 2 to 3 is useful to revealthe irregularity of the surface morphology, and a larger *D* indicates a moreirregular and fragmenting surface [19]. PSD method is based on the assumption that a fractal surface morphologyis superimposed by the infinite frequency mode. The relationship of powerspectrum density$S_\omega$and the corresponding frequency ω depends on *D*. The values of S_ω and ω have relationship as follows:

$$\boldsymbol{S_\omega \propto \omega^{-(5-2D)}}$$

Where D is fractal dimension of the film, the experimental surface is fractal at defined lengthscales of fractal behavior.Outside of these lengths the surface behaves like a flat surface.

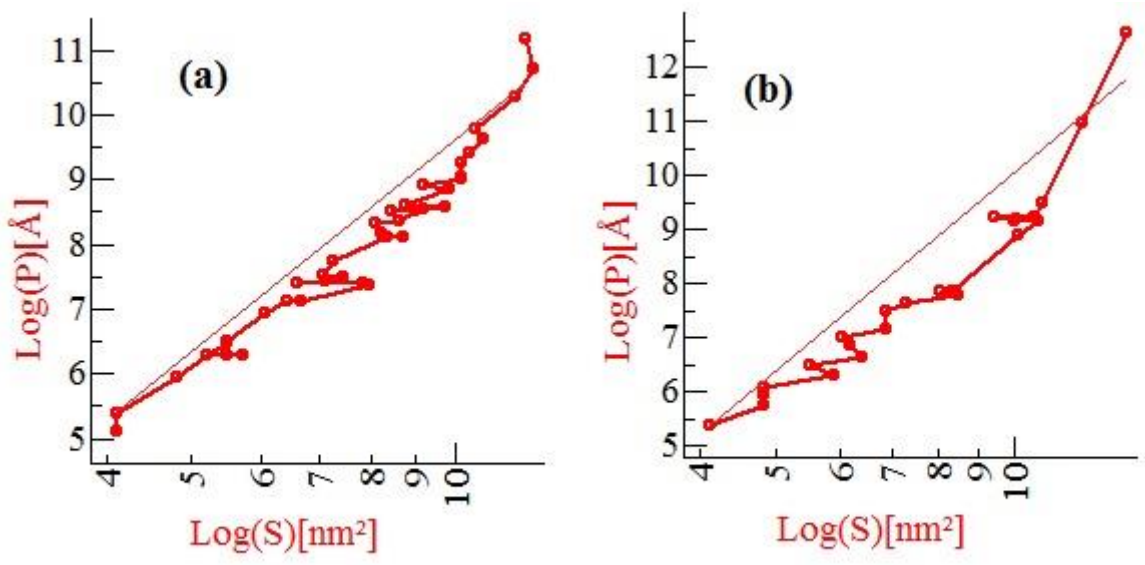

Figure 3 Fractal analyses of BFO thin films annealed at 450 ^{0}C and 500 ^{0}C using Power spectral density (PSD) method.

It can clearly observed fractal dimension values 1.64 and 1.96 be seen that, increasing values plough the fractal dimension. This result indicates that can be employed to describe the variation of theentire grain morphology along direction of the growth. Also, unlikeRMS roughness, the fractal dimension contains spatial information andprofile deviation information. So, the fractal analysis provides a usefuldescription of the irregularities in the surface. As mentioned above,fractal analysis is more accurate than conventional processing due tocalculate the fractal dimension in every scaling range.

4. Conclusion

In present work, we have successfully fabricated BFO thin films prepared by spray pyrolysis method. The XRD confirm single phase formation of BFO thin films with rhombohedral crystal structurewith R-3m space group. The average crystallite sizes as calculated using Scherer's equation found to be in the range of ~15 to 20 nm. The crystallite size and microstrain as calculated from Williamson-Hall methods were found to be ~17.67 nm, 22.35 nm 28.54 nm and 0.028, 0.021 respectively.The RMS surface roughness increases from ~4.56 nm to 7.68 nm with increase the annealing temperature indicates modified the crystal structure of thin films. The fractal dimension values observed from AFM image and found to be 1.64 and 1.96 be seen that, increasing the fractal dimensionwith increasing annealing temperature from 450 °C to 500 °C of sample. This result can be employed to describe the variation of theentire grain morphology along direction of the growth. Also, unlikeRMS roughness, the fractal dimension contains spatial information andprofile deviation information.Thedecrement in RMS surface roughness by increasing annealing temperature with increasing annealing temperature from 450 °C to 500 °C of BFO sampleindicates that the material can have potential applications multiferroic materials baseddevices.

Acknowledgements

The authors are highly thankful to Department of Physics,University of Lucknow, Lucknow for providing X-RD and AFM measurement.

References

[1] G. Lawes and G. Srinivasan, Introduction to magnetoelectric coupling and multiferroic films, J. Phys. D Appl. Phys. 44 (2011) 243001–243022.

[2] J. Ma, J. Hu, Z. Li, and C.W. Nan, Recent progress in multiferroic magnetoelectric composites:From bulk to thin films, Adv. Mater. 23(9) (2011) 1062–1087.
[3] C.C. Zhou, B.C. Luo, K.X. Jin, X.S. Cao, and C.L. Chen, Magnetic and dielectric properties of $BiFeO_3$–$La_{1/3}Sr_{2/3}MnO_3$ hybrid composite ceramics, Solid StateCommun. 150 (2010) 1334-1337.
[4] A.K. Singh, S.D. Kaushik, B. Kumar, P.K. Mishra, A. Venimadhav, V. Siruguri, and S. Patnaik, Substantial magnetoelectric coupling near room temperature in $Bi_2Fe_4O_9$, App.Phys. Lett. 92 (2008) 132910-132913.
[5] H. Koizumi, N. Niizeki, and T. Ikeda, An X-ray study on Bi_2O_3–Fe_2O_3 system, Jpn. J. Appl. Phys. 3 (1964) 495-496.
[6] T. Liu, Y. Xu, and C. Zeng, Synthesis of $Bi_2Fe_4O_9$via PVA sol–gel route, Mater. Sci.Eng. B 176 (2011) 535-539.
[7] Z. Yang, Y. Huang, B. Dong, H.L. Li, and S.Q. Shi, Densely packed single-crystal $Bi_2Fe_4O_9$ nanowires fabricated from a template-induced sol–gel route, J. Solid State Chem. 179 (2006) 3324-3329.
[8] Y. Xiong, M.Z. Wu, Z. M. Peng, N. Jiang and Q.W. Chen, Hydrothermal synthesis andcharacterization of $Bi_2Fe_4O_9$ nanoparticles, Chem. Lett. 33 (2004) 502–503.
[9] Y. G. Wang, G. Xu, L. L. Yang, Z. H. Ren, X. Wei, W. J. Weng, P. Y. Du, G. Shen andG. R. Han, Low temperature polymer assisted hydrothermal synthesis of bismuth ferrite nanoparticles, Ceram. Int. 35 (2009) 51–53.
[10] R.R. Awasthi, B. Das, Structural transition and tunable optical, morphological and magnetic properties of Mn-doped $BiFeO_3$ films, Optik 194 (2019) 162973.
[11] R.R. Awasthi, K. Asokan, B. Das,Structural, dielectric and magnetic domains properties of Mn-doped $BiFeO_3$ materials, International Journal of Applied Ceramic Technology 17 (2020) 1410.
[12] H. Naganuma, J. Miura, and S. Okamura, Ferroelectric, Electrical and Magnetic Properties of Cr, Mn, Co, Ni, Cu Added Polycrystalline $BiFeO_3$ films, Appl. Phys. Lett. 93 (2008) 052901.
[13] R.R. Awasthi, K. Asokan, B. Das, Effect of molar concentration on structural, magnetic domain and optical properties of $BiFeO_3$ thin filmsApplied Physics A 125 (2019) 338.
[14] R.R. Awasthi, B. Das,Effect of temperature on physical properties of $Bi_2Fe_4O_9$ polycrystalline materials, Journal of the Australian Ceramic Society56 (1) (2020) 243.
[15] R.R. Awasthi,S.K. Trivedi, V.S. Chandel, M. Shariq, H.J. Alathlawi,S.P. Singh,Effect of Zn doping on structural/microstructural, surface topography, and dielectric properties of $Bi_2Fe_4O_9$ polycrystalline nanomaterials. ACS omega. 8(2023)15960-15967.
[16] K.C. Dubey, A Zaidi, R.R Awasthi, Environmentally benign structural, topographic, and sensing properties of pure and Al-doped ZnO thin films. ACS omega. 7 (2022)28946-28954.
[17] A Zaidi, K. Tiwari,R.R Awasthi, K.C. Dubey, Effect of sintering temperature on the structural, morphological and humidity sensing properties of ZnO nanostructure. Journal of Ovonic Research 19 (2023) 411-419.
[18] A Zaidi, K. Tiwari,R.R Awasthi, K.C. Dubey, Effect of pH values on the structural, morphological and sensing properties of ZnO nanostructure. Chalcogenide Letters 20 (2023) 33-41.
[19] C.L. Jing, W. Tang, Ga-doped ZnO thin film surface characterization by wavelet and fractal analysis, Appl. Surf. Sci., 364 (2016) 843-849.