

## Supporting Information

### Interband Electronic Transitions and Optical Phonon modes in Size dependent Multiferroic BiFeO<sub>3</sub> Nanoparticles

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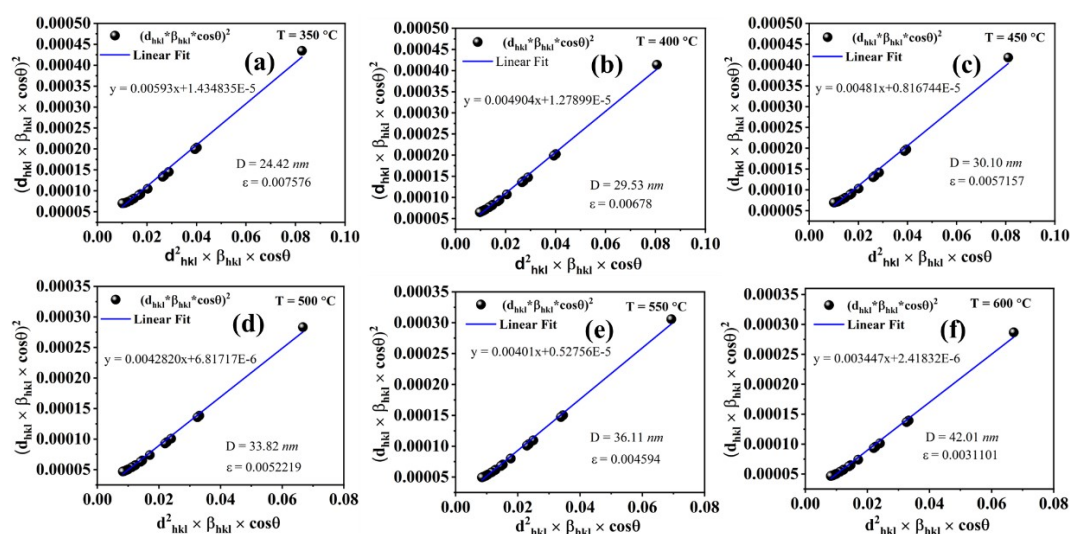
**Table S1:** Structural parameters obtained from Rietveld refinement of BiFeO<sub>3</sub> nanoparticles annealed at different temperature.

Sample (BiFeO <sub>3</sub> NPs)	Phase	Cell parameters	Atom	x	y	z	B <sub>iso</sub> (Å <sup>2</sup> )	Occupancy	R-factor
T = 350 °C	R3C	$a = 5.579012 \text{ \AA}$ , $b = 5.579012 \text{ \AA}$ , $c = 13.861478 \text{ \AA}$ , $\alpha = 90^\circ$ , $\beta = 90^\circ$ , $\gamma = 120^\circ$	Bi (6a)	0.00000	0.00000	0.00041	0.07295	1	$R_p = 17.7$
			Fe (6a)	0.00000	0.00000	0.22151	0.11845	1	$R_{wp} = 14.9$
			O (18a)	0.44689	0.01224	0.95136	0.14897	3	$\chi^2 = 3.44$
T = 400 °C	R3C	$a = 5.577868 \text{ \AA}$ , $b = 5.577868 \text{ \AA}$ , $c = 13.864196 \text{ \AA}$ , $\alpha = 90^\circ$ , $\beta = 90^\circ$ , $\gamma = 120^\circ$	Bi (6a)	0.00000	0.00000	0.00801	0.07180	1	$R_p = 15.6$
			Fe (6a)	0.00000	0.00000	0.23027	0.14189	1	$R_{wp} = 12.9$
			O (18a)	0.44731	0.01812	0.95958	0.13933	3	$\chi^2 = 2.93$
T = 450 °C	R3C	$a = 5.577497 \text{ \AA}$ , $b = 5.577497 \text{ \AA}$ , $c = 13.863589 \text{ \AA}$ , $\alpha = 90^\circ$ , $\beta = 90^\circ$ , $\gamma = 120^\circ$	Bi (6a)	0.00000	0.00000	0.00908	0.07110	1	$R_p = 15.1$
			Fe (6a)	0.00000	0.00000	0.23133	0.14573	1	$R_{wp} = 12.8$
			O (18a)	0.44414	0.01034	0.96011	0.10811	3	$\chi^2 = 3.19$
T = 500 °C	R3C	$a = 5.577722 \text{ \AA}$ , $b = 5.577722 \text{ \AA}$ , $c = 13.865355 \text{ \AA}$ , $\alpha = 90^\circ$ , $\beta = 90^\circ$ , $\gamma = 120^\circ$	Bi (6a)	0.00000	0.00000	0.00940	0.08350	1	$R_p = 15.4$
			Fe (6a)	0.00000	0.00000	0.23128	0.13815	1	$R_{wp} = 13.3$
			O (18a)	0.44444	0.00840	0.96013	0.10442	3	$\chi^2 = 3.51$
T = 550 °C	R3C	$a = 5.57868 \text{ \AA}$ , $b = 5.57868 \text{ \AA}$ , $c = 13.870449 \text{ \AA}$ , $\alpha = 90^\circ$ , $\beta = 90^\circ$ , $\gamma = 120^\circ$	Bi (6a)	0.00000	0.00000	0.00929	0.09085	1	$R_p = 16.4$
			Fe (6a)	0.00000	0.00000	0.23086	0.12411	1	$R_{wp} = 13.8$
			O (18a)	0.44604	0.01220	0.96104	0.09538	3	$\chi^2 = 3.07$

T = 600 °C	R3C	$a = 5.57915 \text{ \AA}$ , $b = 5.57915 \text{ \AA}$ , $c = 13.87190 \text{ \AA}$ , $\alpha = 90^\circ$ , $\beta = 90^\circ$ , $\gamma = 120^\circ$	Bi (6a)	0.00000	0.00000	0.00884	0.09709	1	$R_p = 17.7$
			Fe (6a)	0.00000	0.00000	0.23019	0.12469	1	$R_{wp} = 14.8$
			O (18a)	0.44531	0.01136	0.96117	0.07228	3	$\chi^2 = 3.43$

**Table S2:** Rhombohedral lattice parameters of BiFeO<sub>3</sub> nanoparticles annealed at different temperature.

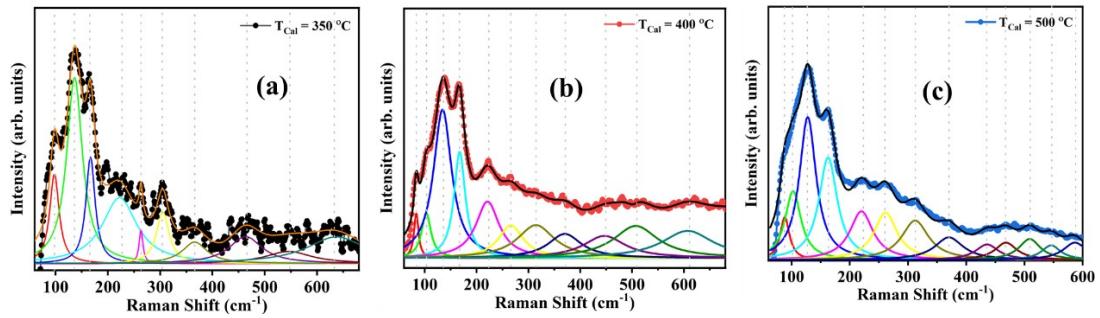
T <sub>Calculation</sub>	350 °C	400 °C	450 °C	500 °C	550 °C	600 °C
$a_{rh}$ (Å)	5.632419	5.632776	5.632493	5.63305	5.634757	5.635312
$\alpha_{rh}$ (°)	59.37366	59.35612	59.35506	59.35124	59.34267	59.34174



**Figure S1.** Modified W-H plot of BFO NPs annealed at different temperature, with inserted average crystallite size and lattice strain.



modes	$T_{\text{Calcination}}$ on = 350°C	= 400 °C	= 450 °C	= 500 °C	= 550 °C	= 600 °C	<i>B.K Das et al.)</i> <sup>1</sup>	<i>P. Chen et al.)</i> <sup>2</sup>
A1(TO3)	380.18 ( $\pm 0.73$ )	379.59 ( $\pm 0.29$ )	380.23 ( $\pm 0.71$ )	379.94 ( $\pm 0.26$ )	380.18 ( $\pm 1.52$ )	380.77 ( $\pm 0.25$ )	319	318.7
E(TO6)	387.49 ( $\pm 0.40$ )	389.59 ( $\pm 0.57$ )	387.61 ( $\pm 0.34$ )	389.33 ( $\pm 1.26$ )	389.59 ( $\pm 0.26$ )	389.71 ( $\pm 1.18$ )	356	351.8
E(TO7)	399.07 ( $\pm 0.89$ )	401.85 ( $\pm 0.34$ )	399.006 ( $\pm 2.14$ )	409.12 ( $\pm 0.86$ )	409.88 ( $\pm 0.92$ )	409.95 ( $\pm 0.75$ )	372	385.5
E(TO8)	445.44 ( $\pm 2.47$ )	448.47 ( $\pm 0.84$ )	443.03 ( $\pm 2.43$ )	444.93 ( $\pm 1.67$ )	442.42 ( $\pm 1.27$ )	442.67 ( $\pm 1.32$ )	442	444.1
E(TO9)	534.67 ( $\pm 1.92$ )	540.67 ( $\pm 5.60$ )	534.68 ( $\pm 1.90$ )	540.04 ( $\pm 4.63$ )	540.95 ( $\pm 4.61$ )	542.67 ( $\pm 3.90$ )	520	536.8
A1(TO4)	568.62 ( $\pm 1.64$ )	579.96 ( $\pm 2.84$ )	568.70 ( $\pm 1.90$ )	579.83 ( $\pm 3.02$ )	580.67 ( $\pm 2.71$ )	582.51 ( $\pm 2.35$ )	547	575.4

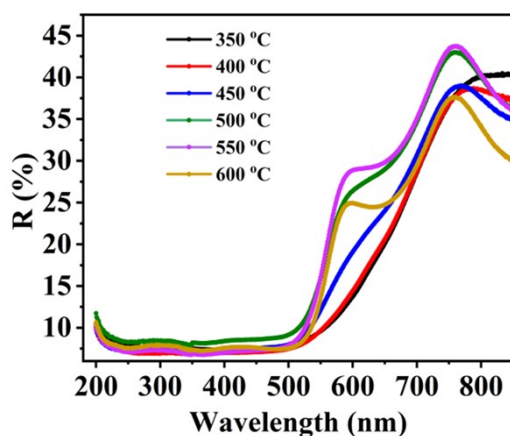


**Figure S4:** Fitted Raman plot of 350 °C (a), 400 °C (b) and 500 °C (c) annealed BiFeO<sub>3</sub> nanoparticles.

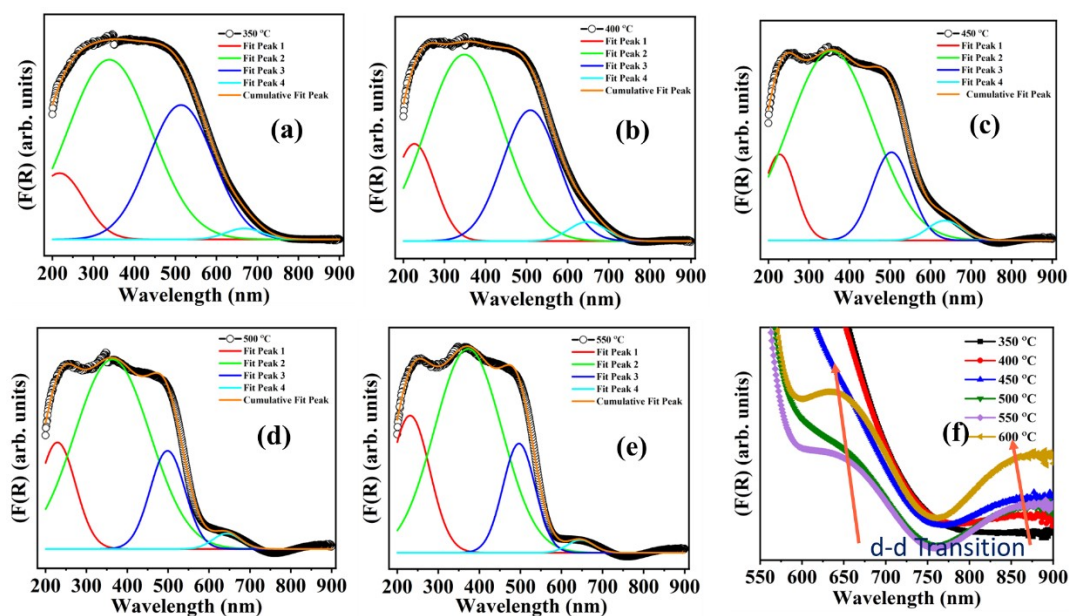
**Table S4:** List of room temperature Raman modes from different annealed BiFeO<sub>3</sub> nanoparticles sample.

Raman Shift (mode)	$T_{\text{Calcination}} = 350 \text{ }^\circ\text{C}$	$T_{\text{Calcination}} = 400 \text{ }^\circ\text{C}$	$T_{\text{Calcination}} = 500 \text{ }^\circ\text{C}$	$T_{\text{Calcination}} = 600 \text{ }^\circ\text{C}$
E(TO1)	-	83.60	88.20	83.78
E(TO2)	97.70	102.91	102.43	108.23
A1(TO <sub>1</sub> )	136.22	136.89	127.66	136.49
E(TO3)	166.68	167.71	162.66	166.90
E(TO4)	222.38	223.83	223.37	220.05

A1(TO2)	263.28	264.82	259.45	262.55
E(TO5)	304.83	315.011	312.18	313.18
A1(TO3)	366.01	371.13	370.22	371.69
E(TO6)	-	446.33	435.71	429.60
E(TO7)	463.47	-	468.17	468.62
E(TO8)	545.83	508.53	508.99	529.77
E(TO9)	-	-	545.81	568.03
A1(TO4)	637.08	611.86	586.73	605.13



**Figure S5.** UV-Vis Reflectance versus Wavelength plot of different annealed BiFeO<sub>3</sub> nanoparticles



**Figure S6:** (a-e) Plot of Kubelka-Munk function (F(R)) with the wavelength of BiFeO<sub>3</sub> nanoparticles ( $T_{\text{Calcination}} = 350\text{ }^{\circ}\text{C}, 400\text{ }^{\circ}\text{C}, 450\text{ }^{\circ}\text{C}, 500\text{ }^{\circ}\text{C}, 550\text{ }^{\circ}\text{C}$ ) and (f) enlarge view of F(R) vs. wavelength, showing shifting of d-d transition to lower wavelength.

## Reference

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- 2 P. Chen, X. Xu, C. Koenigsmann, A. C. Santulli, S. S. Wong and J. L. Musfeldt, *Nano Lett.*, 2010, **10**, 4526–4532.