Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Substitution driven Structural and Magnetic Transformation in Ca-doped $BiFeO_3$ nanoparticles

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TABLE S1: Rietveld refined parameters of $Bi_{1-x}Ca_xFeO_3$ nanostructured samples.

Samples	Lattice parameters	Atoms	Positions	x	y	z	R-factors (%)
x=0	a =5.5751 (Å)	Fe	6a	0.0	0.0	0.0190	R_{wp} = 3.17
	c =13.8590(Å)	Bi	6a	0.0	0.0	0.29745	R_p = 2.49
R3c	V = 373.061 (Å^3)	O	18b	0.2307	0.3581	0.0833	R_f = 1.75
							R_{Bragg} = 1.17
x=0.05	a = 5.5704 (Å)	Fe	6a	0.0	0.0	-0.1785	R_{wp} = 3.36
***R3c* (95.48%)**	c = 13.8243 (Å)	Bi/Ca	6a	0.0	0.0	0.2041	R_p = 2.67
	V = 371.485 (Å^3)	O	18b	0.1023	0.2921	0.0833	R_{fl} = 1.45
***Pnma* (4.52%)**	a = 5.859(Å)	Bi/Ca	4c	0.0294	0.25	0.9686	R_{Bragg1} = 1.75
	b = 7.8276(Å)	Fe	4b	0	0	0.5	$R_{f\,2}$ = 4.61
	c = 5.5830 (Å)	O	4c	0.4834	0.25	0.0725	R_{Bragg2} = 3.81
	V = 244.118 (Å^3)	O	8d	0.0539	0.5035	0.1902	
x=0.10	a = 5.5748 (Å)	Fe	6a	0.0	0.0	-0.1903	R_{wp} = 3.5
***R3c* (74.89%)**	c = 13.8169 (Å)	Bi/Ca	6a	0.0	0.0	0.2052	R_p = 2.78
	V = 371.889 (Å^3)	O	18b	0.0916	0.3112	0.0833	R_{fl} = 1.11
***Pnma* (25.11%)**	a = 5.5763 (Å)	Bi/Ca	4c	-0.014	0.25	0.9858	R_{Bragg1} = 1.35
	b = 7.8303 (Å)	Fe	4b	0	0	0.5	$R_{f\,2}$ = 2.48
	c = 5.5748 (Å)	O	4c	0.5011	0.25	-0.0143	R_{Bragg2} = 2.59
	V = 243.418 (Å^3)	O	8d	0.1792	0.4889	0.2202	
x=0.15	a = 5.5621 (Å)	Fe	6a	0.0	0.0	-0.0188	R_{wp} = 3.45
***R3c* (57.02%)**	c = 13.8167 (Å)	Bi/Ca	6a	0.0	0.0	0.2027	R_p = 2.72
	V = 371.902 (Å^3)	O	18b	0.1028	0.2997	0.0833	R_{fl} = 1.81
***Pnma* (42.98%)**	a = 5.5621 (Å)	Bi/Ca	4c	0.01246	0.25	0.9825	R_{Bragg1} = 1.92
	b = 7.827 (Å)	Fe	4b	0	0	0.5	$R_{f\,2}$ = 3.44
	c = 5.5744 (Å)	O	4c	0.4897	0.25	0.0044	R_{Bragg2} = 2.72
	V = 242.68(Å^3)	O	8d	0.28137	0.479	0.2012	
x=0.20	a = 5.5625 (Å)	Fe	6a	0.0	0.0	-0.0131	R_{wp} = 3.38
***R3c* (15.80%)**	c = 13.7995 (Å)	Bi/Ca	6a	0.0	0.0	0.2193	R_p = 2.68
	V = 369.771 (Å^3)	O	18b	0.1028	0.2781	0.0833	R_{fl} = 3.89
***Pnma* (84.20%)**	a = 5.5506 (Å)	Bi/Ca	4c	0.01464	0.25	0.9848	R_{Bragg1} = 4.1
	b = 7.8316 (Å)	Fe	4b	0	0	0.5	$R_{f\,2}$ = 4.77
	c = 5.5541 (Å)	O	4c	0.5049	0.25	0.0108	R_{Bragg2} = 4.10
	V = 241.438(Å^3)	O	8d	0.1664	0.4575	0.1943	

TABLE S2: Raman modes positions and FWHMs of $Bi_{1-x}Ca_xFeO_3$ nanoparticles.

S. No.	Mode	x = 0.0		x = 0.05		x = 0.10		x = 0.15		x = 0.20	
		Center ω_i cm^{-1}	FWHM Γ_i cm^{-1}	Center ω_i cm^{-1}	FWHM Γ_i cm^{-1}	Center ω_i cm^{-1}	FWHM Γ_i cm^{-1}	Center ω_i cm^{-1}	FWHM Γ_i cm^{-1}	Center ω_i cm^{-1}	FWHM Γ_i cm^{-1}
1	E(TO1)	71.1	8.9	66.3	10.6	64.3	14.9	63.4	15.1	63.9	24.5
2	E(LO1)	76.6	5.3	75.7	10.5	75.3	13.3	75.0	16.4	75.0	32.6
3	E(TO2)	139.2	27.7	143.1	41.4	142.7	43.4	144.7	52.1	145.9	51.8
4	A1(TO1)	172.3	10.9	173.1	15.8	172.7	17.7	172.5	19.5	173.4	31.9
5	A1(TO2)	218.4	17.9	219.7	15.7	221.0	22.0	223.8	23.2	223.8	30.9
6	E(TO3)	232.2	23.5	230.7	19.2	236.4	28.9	239.5	21.1	239.1	23.1
7	E(TO4)	261.2	19.3	257.6	32.7	262.4	30.6	258.3	28.6	256.6	17.1
8	E(TO5)	278.1	23.8	278.2	27.3	280.4	29.3	276.9	29.2	276.7	37.9
9	A1(TO3)	302.4	37.3	299.8	41.6	300.0	27.9	296.4	27.4	306.9	27.7
10	E(TO6)	346.6	27.5	353.1	18.1	341.1	34.4	351.3	35.1	-	-
11	E(TO7)	369.7	10.9	371.1	7.0	370.7	13.6	372.5	21.7	-	-
12	E(TO8)	436.3	11.4	441.6	10.9	454.4	29.8	451.1	36.6	465.5	25.7
13	E(LO8)	471.2	32.6	476.8	32.0	479.4	33.7	479.9	34.9	486.5	28.8
14	E(TO9)	524.0	29.6	521.4	42.6	517.7	43.7	515.6	43.0	512.7	35.1
15	A1(TO4)	550.8	30.6	547.9	28.6	540.8	39.6	545.4	46.8	538.2	38.3
16	E(LO9)	608.2	42.9	614.9	48.6	618.6	56.5	621.5	62.0	631.0	70.8
17	-	-	-	660.9	78.1	665.5	79.8	671.8	67.0	684.1	63.3
18	2E(LO8)	938.4	72.9	937.8	87.5	943.1	85.7	957.9	145.95	940.9	143.3
19	2E(TO9)	1038.8	102.7	1034.6	105.7	1036.2	85.8	1035.8	85.2	1030.4	86.2
20	2A1(TO4)	1101.2	58.7	1099.6	63.3	1097.0	57.1	1096.2	66.2	1085.7	67.6
21	2A1(LO4)	1147.6	47.3	1144.4	57.6	1144.6	57.9	1143.5	62.9	1135.8	67.4
22	2E(LO9)	1264.3	142.4	1273.6	151.7	1275.9	159.2	1276.4	164.8	1281.6	200.3