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Supporting Information

Effects of $BiAlO_3$ - Substitution on the Structures and Properties of Antiferroelectric $PbZrO_3$

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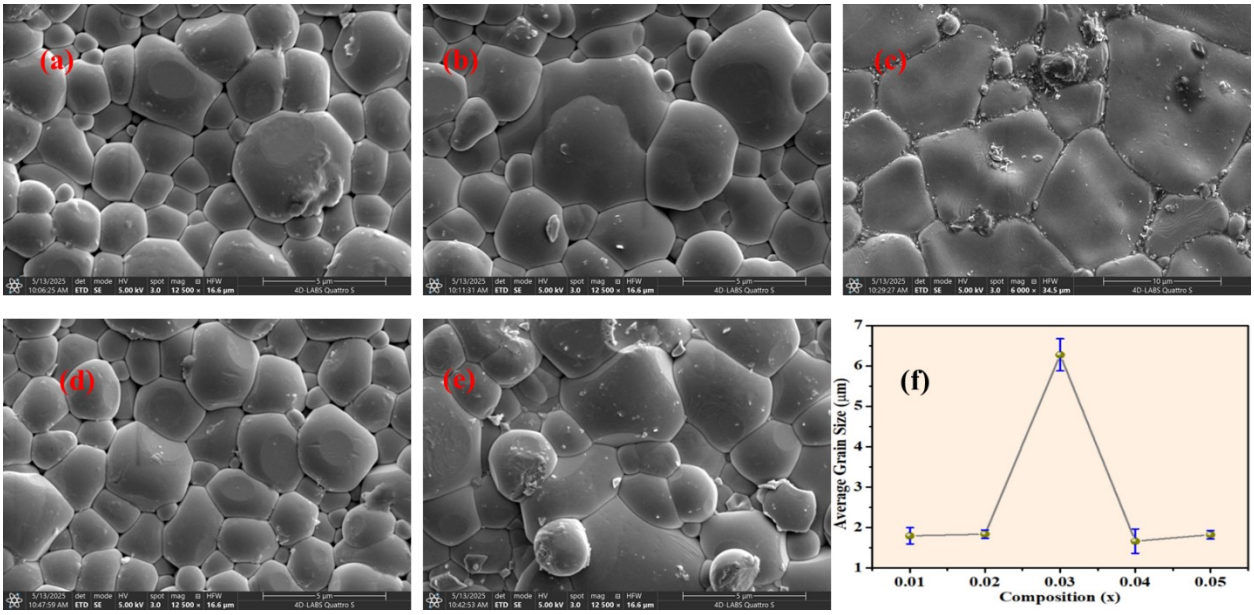


Figure S1. (a-f) SEM images of the surfaces of as sintered (1-x)$PbZrO_3$-x$BiAlO_3$ ceramics: (a) x = 0.01, (b) x = 0.02, (c) x = 0.03, (d) x = 0.04 and (e) x = 0.05. (f) Variation of the average grain size as a function of $BiAlO_3$ concentration, with error bars presented by blue colour.

Figure S1(a-e) shows the microstructure and surface morphology of as-sintered (1-x)$PbZrO_3$-x$BiAlO_3$ ceramics with various compositions. All the micrographs show densely packed grains with clear grain boundaries, no cracks and minimal porosity. The relative density of all the BA-substituted ceramics is found to be ≥ 85 % of the theoritical density. Figure S1(f) presents the average grain sizes of all the prepared compositions, which were calculated with the help of IMAGEJ software. For each sample more than 100 points were taken into the consideration. The largest average grain size of 6.27 μm is found for the x = 0.03 ceramic.

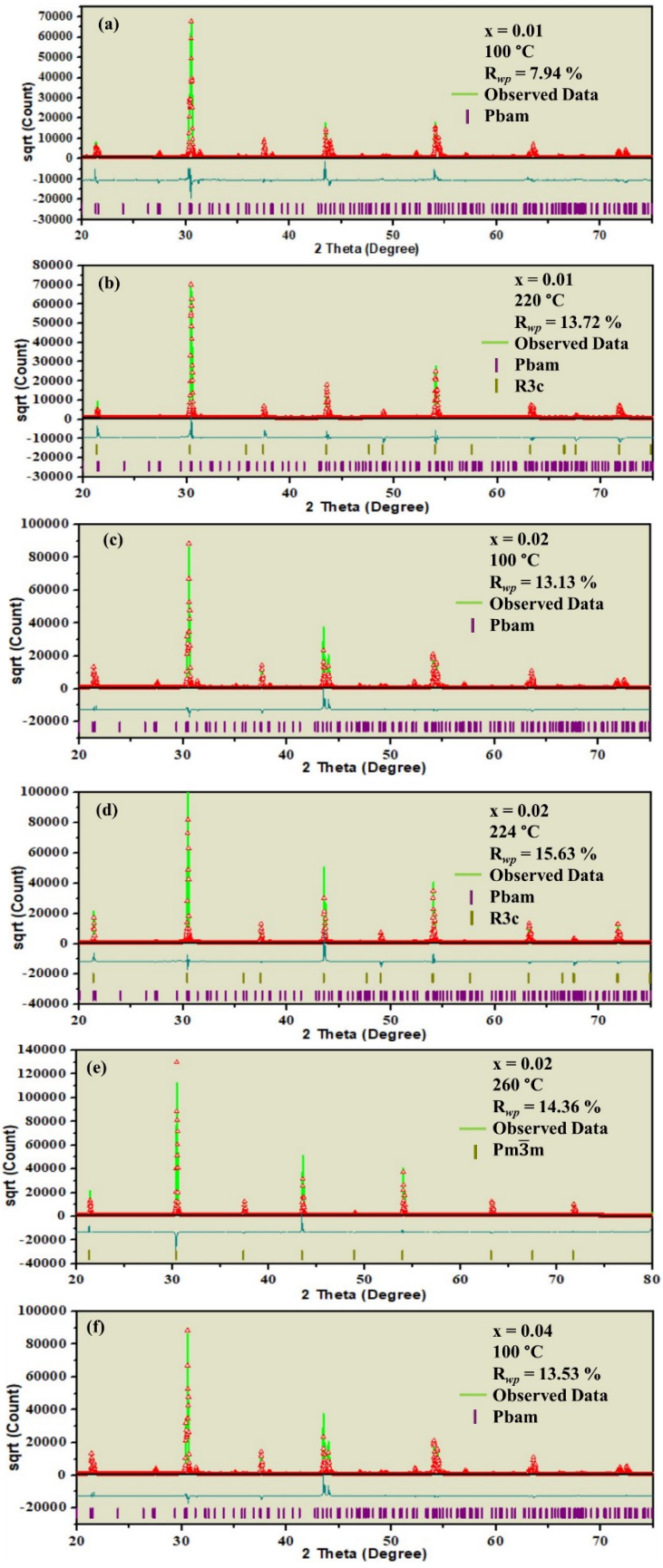
Interstingly, no direct corelation between the grain size and the real part of relative permittivity can be found. While the x = 0.03 with the largest grain size it did not show the highest permittivity at T_{C2}. This observation indicates that the microstructural effects are secondary to the intrinsic, composition-dependent dielectric behavior in the (1-x)$PbZrO_3$-x$BiAlO_3$ solid solution system. The permittivity appears to be more sensitive to compositional modifications which may affect the crystal symmetry and domain configuration.

It is generally believed that a smaller grain size and a denser microstructure would lead to a higher BDS. However, this does not seem to be the case here. The highest BDS is found in x = 0.03 (Fig. 6(f)) with the largest grain size and a dense microstructure (Figure S1(c)).

Table S1. Crystal structure, lattice parameters and unt cell volume of the (1-x)PZ-xBA ceramics at room temperature.

Concentration (x)	Space group	a (Å)	b (Å)	c (Å)	Vol (Å)^3

0.00	Pbam	5.887 (5)	11.797 (5)	8.234 (5)	571.902 (7)
0.01	Pbam	5.878 (3)	11.774 (6)	8.222 (4)	569.065 (6)
0.02	Pbam	5.876 (4)	11.775 (8)	8.221 (6)	568.899 (7)
0.03	Pbam	5.876 (3)	11.773 (8)	8.222 (6)	568.843 (6)
0.04	Pbam	5.876 (3)	11.772 (8)	8.222 (6)	568.797 (7)
0.05	Pbam	5.876 (5)	11.770 (1)	8.222 (9)	568.633 (6)


(a)
x = 0.01
100 °C
R_{wp} = 7.94 %
Observed Data
Pbam
(b)
x = 0.01
220 °C
R_{wp} = 13.72 %
Observed Data
Pbam
R3c
(c)
x = 0.02
100 °C
R_{wp} = 13.13 %
Observed Data
Pbam
(d)
x = 0.02
224 °C
R_{wp} = 15.63 %
Observed Data
Pbam
R3c
(e)
x = 0.02
260 °C
R_{wp} = 14.36 %
Observed Data
$Pm\bar{3}m$
(f)
x = 0.04
100 °C
R_{wp} = 13.53 %
Observed Data
Pbam
sqrt (Count)
2 Theta (Degree)

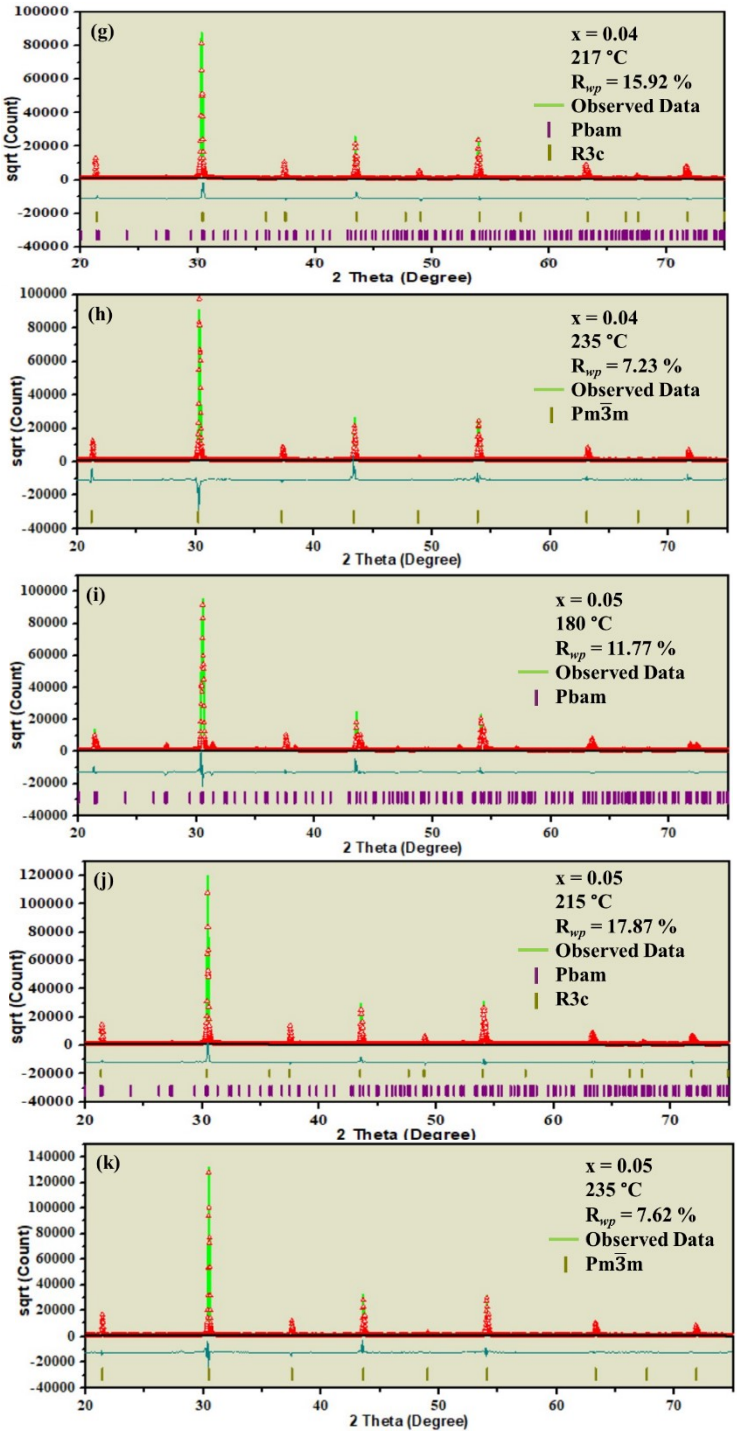


Figure S2. (a-k) Rietveld refinement results of the X-ray powder diffraction patterns of x = 0.01, 0.02, 0.04 and 0.05 ceramic measured at different temperatures. The Pbam space group is used to refine the data below T_{C1}. The $Pm\bar{3}m$ symmetry is used to refine the data above T_{C2}. For the intermediate phase the refinement is performed by using a combination of R3c and Pbam phases.

Table S2. Rietveld refinement parameters and lattice parameters of (1-x)PZ-xBA at various temperatures.

Composition	Temperature (°C)	Symmetry	Lattice parameters (a,b,c) (Å)	Volume $(Å)^3$	Phase fraction
x = 0.01	100	Pbam	a = 5.8766 (8) b = 11.7657 (6) c = 8.2321 (9)	569.205	
x = 0.01	220	Pbam + R3c	a = 5.8745 (7) b = 5.8745 (9) c = 14.3947 (2)	430.220	Pbam = 67 % R3c = 32 %
x= 0.02	100	Pbam	a = 5.8766 (3) b = 11.7653 (5) c = 8.2312 (7)	569.121	
x = 0.02	224	Pbam + R3c	a = 5.8742 (6) b = 5.8742 (6) c = 14.3961 (5)	430.218	Pbam = 62 % R3c = 37 %
x = 0.02	260	$Pm\bar{3}m$	a = 4.1555 (2) b = 4.1555 (2) c = 4.1555 (2)	71.759	
x= 0.03	80	Pbam	a = 5.8786 (7) b = 11.7744 (8) c = 8.2323 (6)	569.831	
x= 0.03	210	Pbam + R3c	a = 5.8731 (4) b = 5.8731 (4) c = 14.3950 (1)	430.023	Pbam = 58 % R3c = 42 %
x= 0.03	250	$Pm\bar{3}m$	a = 4.1550 (2) b = 4.1550 (2) c = 4.1550 (2)	71.732	
x= 0.04	100	Pbam	a = 5.8759 (5) b = 11.7596 (8) c = 8.2506 (4)	570.101	
x= 0.04	217	Pbam + R3c	a = 5.8729 (7) b = 5.8729 (7) c = 14.3915 (4)	429.890	Pbam = 56 % R3c = 43 %
x= 0.04	235	$Pm\bar{3}m$	a = 4.1543 (6) b = 4.1543 (5) c = 4.1543 (3)	71.699	
x= 0.05	180	Pbam	a = 5.8769 (1) b = 11.7604 (2) c = 8.2517 (7)	570.323	
x= 0.05	215	Pbam + R3c	a = 5.8759 (3) b = 5.8795 (1) c = 14.3114 (4)	427.922	Pbam = 54 % R3c = 45 %
x= 0.05	235	$Pm\bar{3}m$	a = 4.1542 (2) b = 4.1542 (2) c = 4.1542 (2)	71.695	

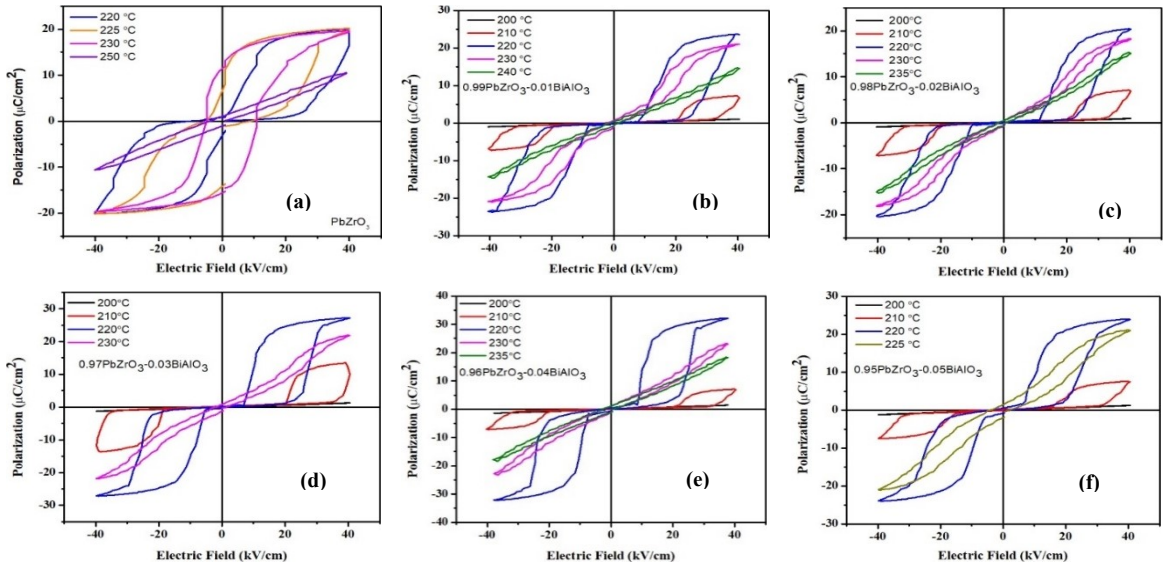


Figure S3. (a-f) Polarization-electric field (P-E) relations measured under electric fields of ± 40 kV/cm at 10 Hz frequency at various temperatures between 200 and 250 °C.