

Supplementary Information

Electron-pinned Defect Dipoles in (Li, Al) Co-doped ZnO Ceramics with Colossal Dielectric Permittivity

Dong Huang¹, Wen-Long Li², Zhi-Fu Liu^{*2}, Yong-Xiang Li^{*2}, Cuong Ton-That³, Jiaqi Cheng⁴, Wallace C. H. Choy⁴, Francis Chi-Chung Ling^{*1}

¹ Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, China

² CAS Key Lab of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, China

³ School of Mathematical and Physical Sciences, University of Technology Sydney, NSW, 2007, Australia.

⁴ Department of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China

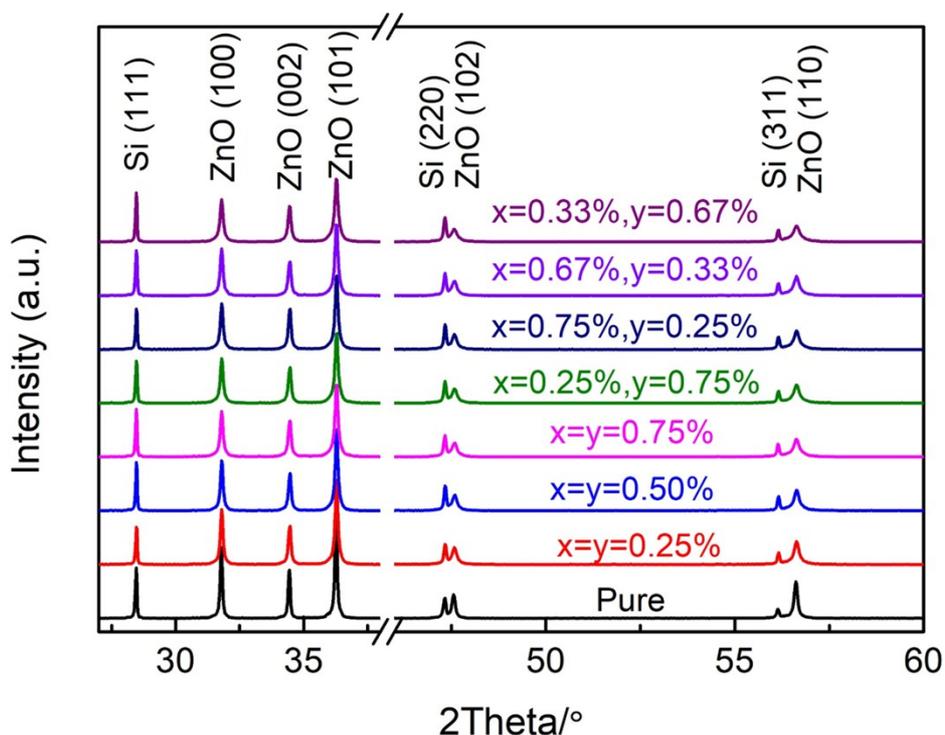


Figure S1 The XRD spectra of the (Li_x, Al_y)Zn_{1-x-y}O ceramics sintered at 1548 K for various values of x and y between 0 and 0.75. The black spectrum is pure ZnO. An equal amount of Si is added to each ceramic disc for calibration and used as XRD reference.

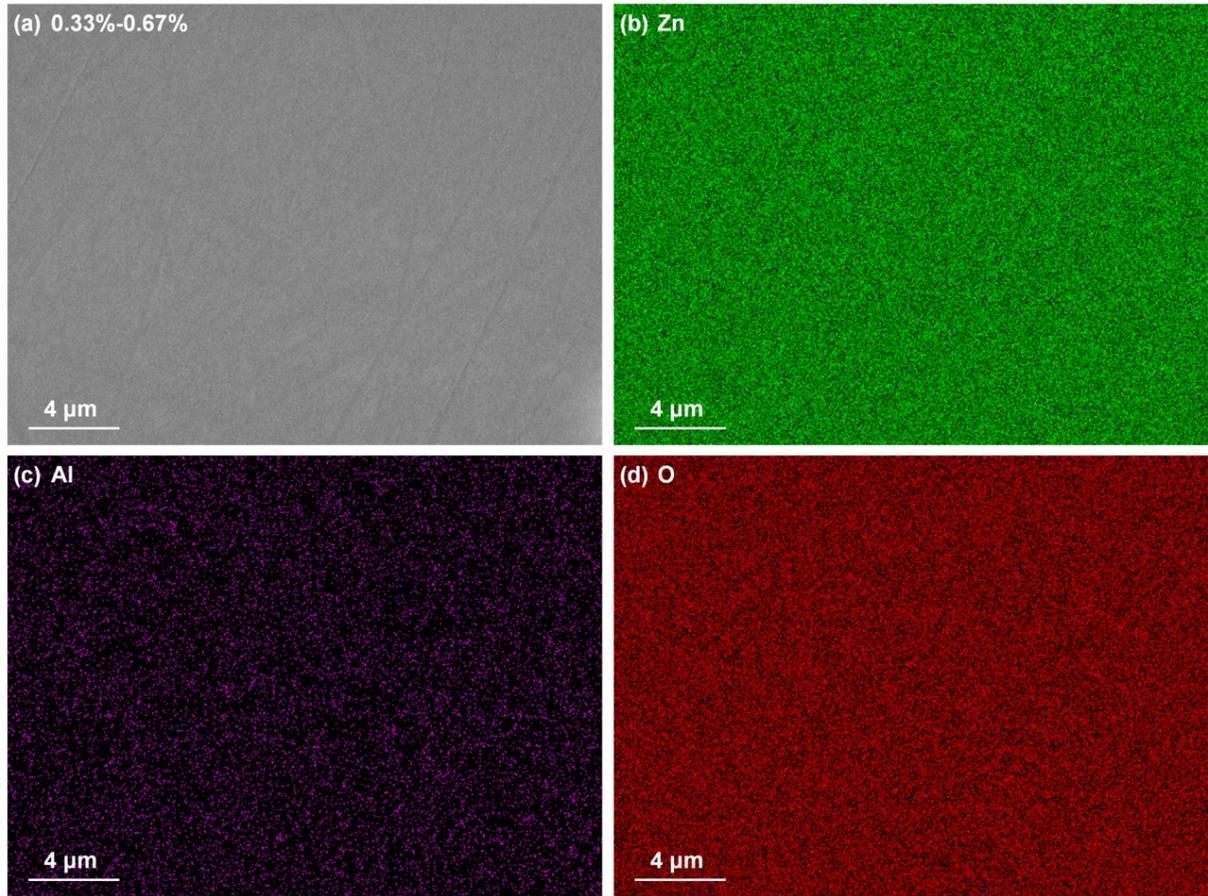


Figure S2 SEM image and EDX maps of Zn, Al and O in the LAZ ceramic before annealing.

Table S1 The dielectric property of the $(Li_x, Al_y) Zn_{1-x-y}O$ samples at 1 kHz with different x and y sintered at different temperature.

Li/Al(x/y %)	1473 K		1498 K		1523 K		1548 K	
	$\tan\delta$	ϵ	$\tan\delta$	ϵ	$\tan\delta$	ϵ	$\tan\delta$	ϵ
0.25/0.25	0.30	6748	0.22	6214	0.23	7695	0.36	13735
0.50/0.50	0.51	7063	0.40	10771	0.77	8099	0.92	10477
0.75/0.75	0.20	3756	0.18	4035	0.18	5542	0.25	8949
0.25/0.75	0.30	7030	0.20	4710	0.21	5081	0.15	7484
0.75/0.25	0.31	8485	0.41	10821	0.39	11646	0.55	17186
0.33/0.67	0.26	7458	0.27	6384	0.13	7694	0.16	9862
0.67/0.33	0.49	10250	0.41	10739	0.38	13619	0.46	14565

Table S2 The average grain size and the dielectric properties of the as-grown LAZ, AZ, LZ samples.

Sample	Average grain size(μm)	Dielectric constant	Dielectric Loss
(Li, Al) co-doped ZnO	3~6	9862	0.16
Al doped ZnO	5~8	2e5	1.30
Li doped ZnO	6~10	159	2.17

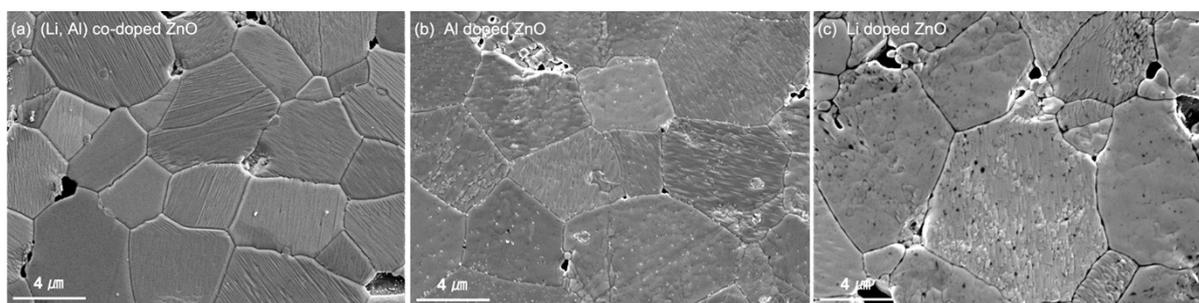


Figure S3 The scanning electron microscopy images of the as-grown samples (a) LAZ, (b) AZ and (c) LZ on the etched surface

The scanning electron microscope images on the etched surface are shown as above in Figure S3, showing that the grains are in pentagonal and hexagonal patterns. The average grain size has been obtained based on intercept method in Table S2. The (Li, Al) co-doped ZnO (LAZ), Al doped ZnO (AZ) and Li doped ZnO (LZ) samples have the grains sizes varying in a relatively narrow range 3-10 micron. However, their dielectric properties show dramatic changes with different dopants. This shows that the grain size does not have a strong correlation with the dielectric constant in our samples.

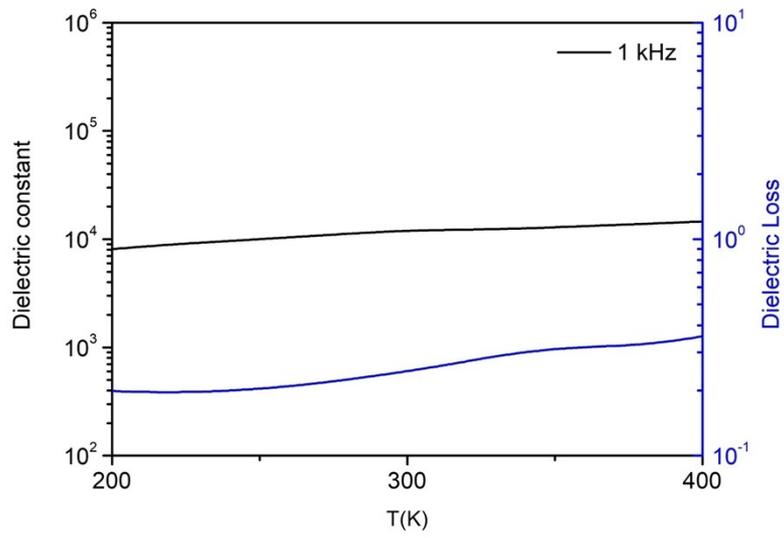


Figure S4 The temperature stability at 1 kHz from 200 to 400 K of (Li, Al) co-doped ZnO.

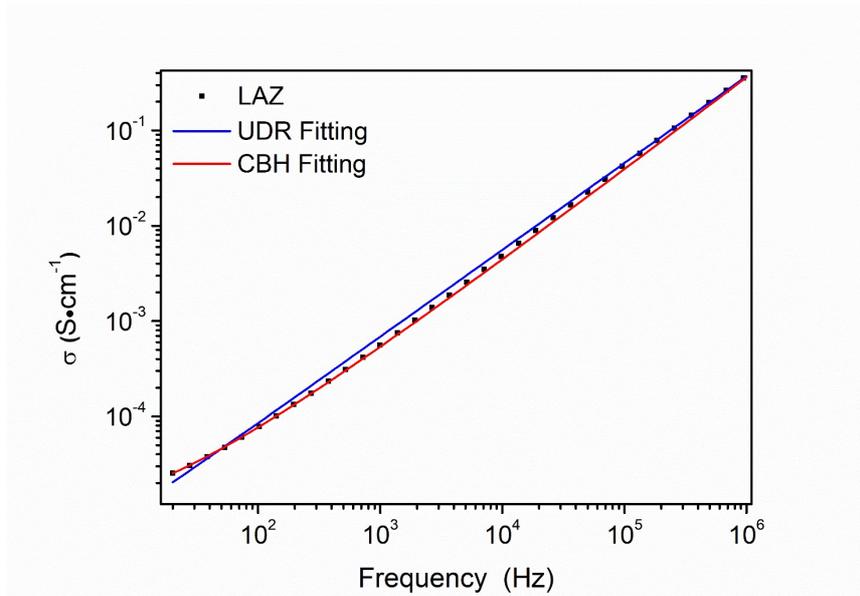


Figure S5 The comparison between the UDR and CBH fitting on σ_{ac} vs frequency of LAZ sample.

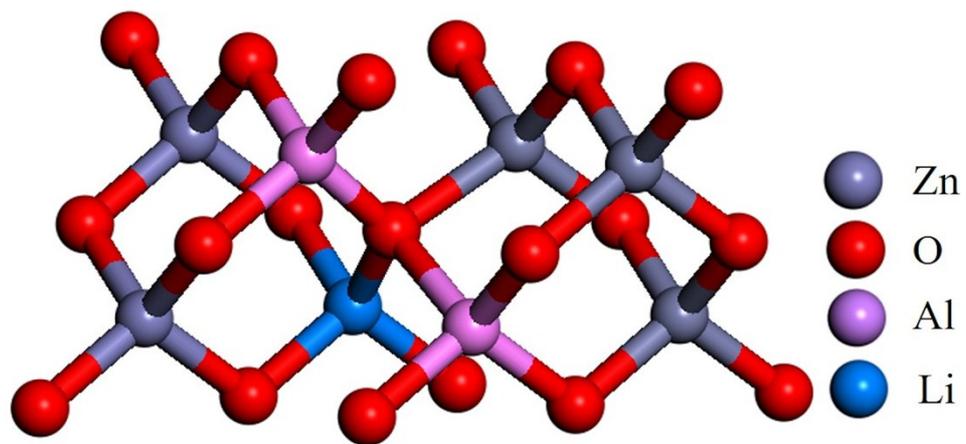


Figure S6 The schematic illustration of $\text{Al}_{\text{Zn}}\text{-Li}_{\text{Zn}}$ defect complex