

Electronic Supplementary Information

Unique pure barium titanate foams with three-dimensional interconnecting pore channels and their high- k cyanate ester resin composites at very low barium titanate loading

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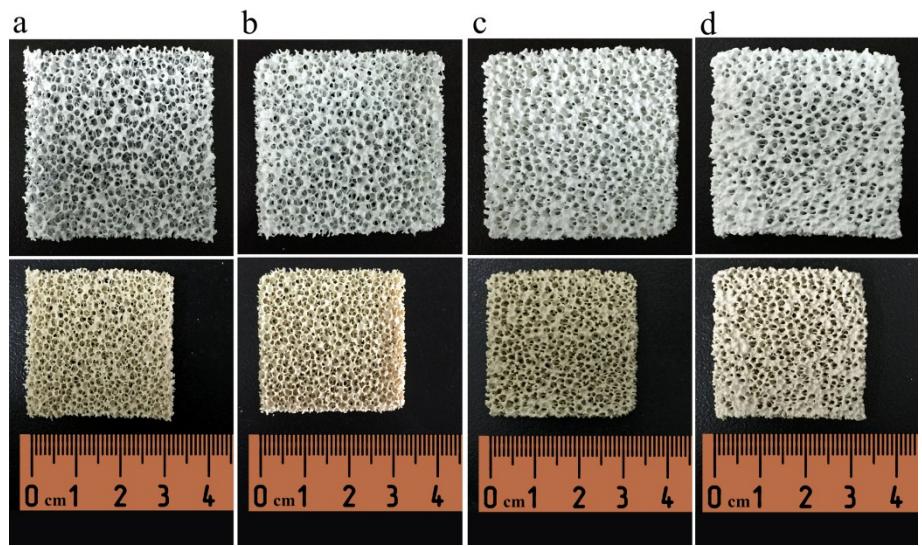


Fig. S1 Digital photos of green bodies (top) and sintered FCs (bottom) at 1200 °C (a: BTF3, b: BTF4, c: BTF5, d: BTF6).

Table S1 Dielectric constants of ceramic/polymer composites ^{a)}

Filler ^{b)}	Filler loading (vol%)	Polymer matrix ^{c)}	Dielectric constant	Frequency (Hz)	Refer
BCZT	61	PVDF	100	1000	[S1]
BSCT	33	PVDF	~50	100	[S2]
BST	55	PVDF	89	100	[S3]
BST	50	P(VDF-TrFE)	~76	100	[S4]
BST	40	P(VDF-CTFE)	70	1000	[S5]
BST	40	P(VDF-CTFE)	~50	100	[S6]
BT	50	CE	~26	100	[S7]
BT	40	CR-S	~80	100	[S8]
BT	50	ENR-50	~50	1000	[S9]
BT	60	epoxy	~40	1000	[S10]
BT	40	epoxy	44	100	[S11]
BT	40	epoxy	~30	100	[S12]
BT	50	EVM	~14.2	100	[S13]
BT	50	PES	~63	100	[S14]
BT	45	PFCB	~33	1000	[S15]
BT	50	PI	~37	100	[S16]
BT	50	PI	<35	1000	[S17]
BT	50	PI	~24	1000	[S18]
BT	60	PVDF	~100	100	[S19]
BT	55	PVDF	~60	1000	[S20]
BT	50	PVDF	~78	100	[S21]
BT	50	PVDF	53.9	1000	[S22]
BT	50	PVDF	~52	1000	[S23]
BT	45	PVDF	~57	100	[S24]
BT	40	PVDF	~51	1000	[S25]
BT	40	PVDF	~50	1000	[S26]
BT	40	PVDF	~45	1000	[S27]
BT	40	PVDF	~70	100	[S28]
BT	40	PVDF	~40	100	[S29]
BT	40	PVDF	~38	1000	[S30]
BT	30	PVDF	~28	100Hz	[S31]
BT	30	PVDF	22.02	1000	[S32]
BT	40	P(VDF-CTFE)	<80	100	[S33]
BT	50	PVDF-HFP-GMA	~43	1000	[S34]
BT	40	P(VDF-TrFE)	70	1000	[S35]
BT	30	P(VDF-TrFE-CTFE)	~55	1000	[S36]

Table S1 Continued.

Filler	Filler loading (vol%)	Polymer matrix	Dielectric constant	Frequency (Hz)	Refer
BT NWs	30	PVDF	<45	1000	[S37]
BT-OPA	50	P(VDF-HFP)	~25	120	[S38]
BT-PFBPA	50	P(VDF-HFP)	37 ± 2	1000	[S39]
BT-TDPA	40	PVDF	74.9	100	[S40]
BT@TiO ₂	40	P(VDF-HFP)	~73	1000	[S41]
CCTO ^{Semi}	40	PVDF	2.49 × 10 ⁶	100	[S42]
CCTO	55	PVDF	95	100	[S43]
CCTO	40	PVDF	35	100	[S42]
CCTO	30	PVDF	90	100Hz	[S44]
CCTO	50	P(VDF-HFP)	<30	120	[S45]
CCTO	40	epoxy	50	100	[S46]
CCTO	40	PI	49	100	[S47]
CCTO	40	silicone resin	~10	1000	[S48]
CCTO	30	CE	~12	100	[S49]
CCTO-sg	50	PVDF	62.3	100	[S50]
FTN	30	PVDF	~100	100	[S51]
KTNO ^{Semi}	30	PVDF	~200	1000	[S52]
LTNO-0	40	PVDF	~90	100	[S53]
LTNO-1 ^{Semi}	40	PVDF	~600	100	[S53]
PMN-PT	40	P(VDF-TrFE)	~125	100	[S54]
PMN-PT	40	P(VDF-TrFE)	37.3	1000	[S55]
PSTM	50	PEKK	42	1000	[S56]
PZT	70	PVDF	140	100	[S57]
PZT	40	PVDF	~45	1000	[S58]
PZT	40	PVDF	~40	1000	[S59]
PZT	40	PVDF	~36	100	[S28]
PZT	50	P(VDF-CTFE)	80	1000	[S60]
PZT	40	Polyester resin	45	1000	[S61]
SiC	47	P(VDF-CTFE-DB)	83	100	[S62]
TiO ₂	35	PVDF	~13.5	1000	[S63]
BTF	33.5	CE	141.3 117.8	100 1000	This work

- a) The data of high-*k* composites are arranged, while some of them not reported directly in the references are derived from the corresponding curves, the symbol “~” is used to indicate that the datum is an approximate value.
- b) BCZT: Calcium barium zirconate titanate ($\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Zr}_{0.15}\text{Ti}_{0.85}\text{O}_3$).
BSCT: $(\text{Ba}_{0.5}\text{Sr}_{0.4}\text{Ca}_{0.1})\text{TiO}_3$.

- BST: $\text{Ba}_x\text{Sr}_y\text{TiO}_3$.
- BT: Barium titanate.
- BT NWs: Barium titanate nanowires.
- OPA: n-Octylphosphonic acid.
- PFBPA: Pentafluorobenzyl phosphonic acid.
- TDPA: 1-Tetradecylphosphonic acid.
- TiO_2 : Titanium dioxide.
- CCTO ^{Semi}: Calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) with semiconductor feature.
- CCTO: $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$.
- CCTO-sg: $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ were prepared by the sol–gel method.
- FTN: FeTiNbO_6 .
- KTNO: $\text{K}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}\text{O}$.
- KTNO ^{Semi}: $\text{K}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}\text{O}$ with semiconductor feature.
- LTNO: Li and Ti codoped NiO.
- LTNO-0: LTNO sintered at 1250 °C.
- LTNO-1: LTNO used without further sintering.
- LTNO-1 ^{Semi}: LTNO with semiconductor feature.
- PMN–PT: Lead magnesium niobate–lead titanate.
- PSTM: Samarium and manganese modified lead titanate.
- PZT: Lead zirconate titanate.
- SiC: Silicon carbide.
- BTF: Barium titanate foam ceramic.
- c) PVDF: Poly(vinylidene fluoride).
- P(VDF-TrFE): Poly(vinylidenefluoride-trifluoroethylene).
- P(VDF-CTFE): Poly(vinylidene fluoride-chlorotrifluoroethylene).
- CE: Cyanate ester.
- CR-S: Cyanoethylated cellulose polymer
- ENR-50: Epoxidized natural rubber with 50 mol% epoxide.
- EVM: Ethylene vinyl-acetate copolymer.
- PES: Polyethersulfone.
- PFBC: Poly 1,1,1-triphenyl ethane perfluorocyclobutyl ether.
- PI: Polyimide.
- PVDF-HFP-GMA: Poly(vinylidene fluoride-cohexafluoropropylene) functionalized with glycidyl methacrylate.
- P(VDF-TrFE-CTFE): Poly(vinylidene fluoride-*tert*-trifluoroethylene-*tert*-chlorotrifluoroethylene).
- P(VDF-HFP): Poly(vinylidenefluoride-co-hexafluoropropylene).
- PEKK: Polyetherketoneketone.
- P(VDF-CTFE-DB): Poly(vinylidenefluoride-co-chlorotrifluoroethylene) with internal double bonds.

Table S2 Parameters from simulating results for BTFn(1200)/CE, BTfp33.5%/CE and BT33.5%/CE composites

	BTFp33.5%/CE	BT33.5%/CE	BTF3(1200)/CE	BTF4(1200)/CE	BTF5(1200)/CE	BTF6(1200)/CE
R1(Ω)	7.938×10^4	1.902×10^{12}	3.558×10^{10}	1.557×10^9	1.185×10^9	5.108×10^8
C1(F)	7.339×10^{-10}	2.233×10^{-11}	2.408×10^{-11}	2.511×10^{-10}	2.164×10^{-10}	3.081×10^{-10}
R2(Ω)	9.966×10^{20}	1.006×10^{24}	1.946×10^9	8.771×10^8	6.870×10^8	2.550×10^8
C2(F)	/	/	1.326×10^{-11}	1.783×10^{-11}	2.423×10^{-11}	3.906×10^{-11}
CPE(F)	5.720×10^{-12}	2.042×10^{-11}	5.810×10^{-11}	1.258×10^{-10}	1.005×10^{-10}	2.125×10^{-10}
n	0.997	0.993	0.702	0.567	0.703	0.674
Cv(F)	6.092×10^{-12}	2.519×10^{-11}	2.298×10^{-11}	2.342×10^{-11}	3.256×10^{-11}	5.181×10^{-11}
Rt(Ω)	9.966×10^{20}	1.006×10^{24}	3.753×10^{10}	2.434×10^9	1.872×10^9	7.658×10^8
Ct(F)	6.042×10^{-12}	1.184×10^{-11}	1.447×10^{-11}	3.543×10^{-11}	4.498×10^{-11}	7.017×10^{-11}

References

- [S1] B. C. Luo, X. H. Wang, Y. P. Wang and L. T. Li, *J. Mater. Chem. A*, 2014, **2**, 510-519.
- [S2] E. Q. Huang, J. Zhao, J. W. Zha, L. Zhang, R. J. Liao and Z. M. Dang, *J. Appl. Phys.*, 2014, **115**, 194102.
- [S3] K. Li, H. Wang, F. Xiang, W. Liu and H. Yang, *Appl. Phys. Lett.*, 2009, **95**, 202904.
- [S4] S. U. Adikary, H. L. W. Chan, C. L. Choy, B. Sundaravel and I. H. Wilson, *Compos. Sci. Technol.*, 2002, **62**, 2161-2167.
- [S5] L. Zhang, P. Wu, Y. Li, Z. Y. Cheng and J. C. Brewer, *Compos. Part B-Eng.*, 2014, **56**, 284-289.
- [S6] P. Wu, L. Zhang and X. Shan, *Mater. Lett.*, 2015, **159**, 72-75.
- [S7] F. Chao, N. Bowler, X. Tan, G. Liang and M. R. Kessler, *Compos. Part A-Appl. Sci. Manuf.*, 2009, **40**, 1266-1271.
- [S8] C. K. Chiang and R. Popielarz, *Ferroelectrics*, 2002, **275**, 1-9.
- [S9] S. Salaeh, G. Boiteux, P. Cassagnau and C. Nakason, *Int. J. Appl. Ceram. Technol.*, 2015, **12**, 106-115.
- [S10] Z. M. Dang, Y. F. Yu, H. P. Xu and J. Bai, *Compos. Sci. Technol.*, 2008, **68**, 171-177.
- [S11] D. H. Kuo, C. C. Chang, T. Y. Su, W. K. Wang and B. Y. Lin, *Mater. Chem. Phys.*, 2004, **85**, 201-206.
- [S12] R. Ginés, R. Libanori, A. R. Studart, A. Bergamini, M. Motavalli and P. Ermanni, *Compos. Part B-Eng.*, 2015, **72**, 80-86.

- [S13] X. Huang, L. Xie, P. Jiang, G. Wang and F. Liu, *J. Phys. D: Appl. Phys.*, 2009, **42**, 245407.
- [S14] F. J. Wang, W. Li, M. S. Xue, J. P. Yao and J. S. Lu, *Compos. Part B-Eng.*, 2011, **42**, 87-91.
- [S15] I. Vrejoiu, J. D. Pedarnig, M. Dinescu, S. Bauer-Gogonea and D. Bäuerle, *Appl. Phys. A-Mater.*, 2002, **74**, 407-409.
- [S16] S. H. Xie, B. K. Zhu, X. Z. Wei, Z. K. Xu and Y. Y. Xu, *Compos. Part A-Appl. Sci. Manuf.*, 2005, **36**, 1152-1157.
- [S17] B. H. Fan, J. W. Zha, D. R. Wang, J. Zhao and Z. M. Dang, *Appl. Phys. Lett.*, 2012, **100**, 092903.
- [S18] N. G. Devaraju, E. S. Kim and B. I. Lee, *Microelectron. Eng.*, 2005, **82**, 71-83.
- [S19] Y. P. Mao, S. Y. Mao, Z. G. Ye, Z. X. Xie and L. S. Zheng, *J. Appl. Phys.*, 2010, **108**, 014102.
- [S20] K. Yu, Y. Niu, Y. Zhou, Y. Bai, H. Wang and C. Randall, *J. Am. Ceram. Soc.*, 2013, **96**, 2519-2524.
- [S21] Y. H. Li, J. J. Yuan, J. Xue, F. Y. Cai, F. Chen and Q. Fu, *Compos. Sci. Technol.*, 2015, **118**, 198-206.
- [S22] K. Yu, H. Wang, Y. Zhou, Y. Bai and Y. Niu, *J. Appl. Phys.*, 2013, **113**, 034105.
- [S23] K. Yu, Y. Niu, F. Xiang, Y. Zhou, Y. Bai and H. Wang, *J. Appl. Phys.*, 2013, **114**, 174107.
- [S24] J. W. Zha, X. Meng, D. R. Wang, Z. M. Dang and R. K. Y. Li, *Appl. Phys. Lett.*, 2014, **104**, 072906.
- [S25] Y. Niu, K. Yu, Y. Bai, F. Xiang and H. Wang, *RSC Adv.*, 2015, **5**, 64596-64603.
- [S26] Y. Niu, Y. Bai, K. Yu, Y. Wang, F. Xiang and H. Wang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 24168-24176.
- [S27] Z. M. Dang, H. Y. Wang and H. P. Xu, *Appl. Phys. Lett.*, 2006, **89**, 112902.
- [S28] R. Gregorio, M. Cestari and F. E. Bernardino, *J. Mater. Sci.*, 1996, **31**, 2925-2930.
- [S29] Z. M. Dang, L. Z. Fan, Y. Shen and C. W. Nan, *Chem. Phys. Lett.*, 2003, **369**, 95-100.
- [S30] Y. Li, X. Huang, Z. Hu, P. Jiang, S. Li and T. Tanaka, *ACS Appl. Mater. Interfaces*, 2011, **3**, 4396-4403.
- [S31] T. Zhou, J. W. Zha, R. Y. Cui, B. H. Fan, J. K. Yuan and Z. M. Dang, *ACS Appl. Mater. Interfaces*, 2011, **3**, 2184-2188.
- [S32] P. Hu, Y. Shen, Y. Guan, X. Zhang, Y. Lin, Q. Zhang and C. W. Nan, *Adv. Funct. Mater.*, 2014, **24**, 3172-3178.
- [S33] F. Wen, Z. Xu, W. Xia, X. Wei and Z. Zhang, *Polym. Eng. Sci.*, 2013, **53**, 897-904.
- [S34] L. Y. Xie, X. Y. Huang, K. Yang, S. T. Li and P. K. Jiang, *J. Mater. Chem. A*, 2014, **2**, 5244-5251.
- [S35] T. Siponkoski, M. Nelo, J. Peräntie, J. Juuti and H. Jantunen, *Compos. Part B-Eng.*, 2015, **70**, 201-205.
- [S36] J. Li, J. Claude, L. E. Norena-Franco, S. I. Seok and Q. Wang, *Chem. Mater.*, 2008, **20**, 6304-6306.
- [S37] H. Tang, Z. Zhou and H. A. Sodano, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5450-5455.
- [S38] C. Ehrhardt, C. Fettkenhauer, J. Glenneberg, W. Münchgesang, C. Pientschke, T. Großmann, M. Zenkner, G. Wagner, H. S. Leipner, A. Buchsteiner, M. Diestelhorst, S. Lemm, H. Beige and S. G. Ebbinghaus, *Mater. Sci. Eng-B*, 2013, **178**, 881-888.

- [S39] P. Kim, S. C. Jones, P. J. Hotchkiss, J. N. Haddock, B. Kippelen, S. R. Marder and J. W. Perry, *Adv. Mater.*, 2007, **19**, 1001-1005.
- [S40] H. J. Ye, W. Z. Shao and L. Zhen, *Colloids Surf. Physicochem. Eng. Aspects*, 2013, **427**, 19-25.
- [S41] M. Rahimabady, M. S. Mirshekarloo, K. Yao and L. Lu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 16242-16248.
- [S42] W. Yang, S. Yu, R. Sun and R. Du, *Acta Mater.*, 2011, **59**, 5593-5602.
- [S43] P. Thomas, K. T. Varughese, K. Dwarakanath and K. B. R. Varma, *Compos. Sci. Technol.*, 2010, **70**, 539-545.
- [S44] P. Thomas, *eXPRESS Polym. lett.*, 2010, **4**, 632-643.
- [S45] C. Ehrhardt, C. Fettkenhauer, J. Glenneberg, W. Münchgesang, H. S. Leipner, M. Diestelhorst, S. Lemm, H. Beige and S. G. Ebbinghaus, *J. Mater. Chem. A*, 2014, **2**, 2266-2274.
- [S46] B. Shri Prakash and K. B. R. Varma, *Compos. Sci. Technol.*, 2007, **67**, 2363-2368.
- [S47] Z. M. Dang, T. Zhou, S. H. Yao, J. K. Yuan, J. W. Zha, H. T. Song, J. Y. Li, Q. Chen, W. T. Yang and J. Bai, *Adv. Mater.*, 2009, **21**, 2077-2082.
- [S48] S. Babu, K. Singh and A. Govindan, *Appl. Phys. A-Mater.*, 2012, **107**, 697-700.
- [S49] Y. P. Shen, A. J. Gu, G. Z. Liang and L. Yuan, *Compos. Part A-Appl. Sci. Manuf.*, 2010, **41**, 1668-1676.
- [S50] X. Chao, P. Wu, Y. Zhao, P. Liang and Z. Yang, *Journal of Materials Science: Materials in Electronics*, 2015, **26**, 3044-3051.
- [S51] J. Fu, Y. Hou, Q. Wei, M. Zheng, M. Zhu and H. Yan, *J. Appl. Phys.*, 2015, **118**, 235502.
- [S52] D. Bhadra, A. Biswas, S. Sarkar, B. K. Chaudhuri, K. F. Tseng and H. D. Yang, *J. Appl. Phys.*, 2010, **107**, 124115.
- [S53] Z. M. Dang, J. B. Wu, L. Z. Fan and C. W. Nan, *Chem. Phys. Lett.*, 2003, **376**, 389-394.
- [S54] Y. Bai, Z. Y. Cheng, V. Bharti, H. S. Xu and Q. M. Zhang, *Appl. Phys. Lett.*, 2000, **76**, 3804-3806.
- [S55] K. H. Lam and H. L. W. Chan, *Compos. Sci. Technol.*, 2005, **65**, 1107-1111.
- [S56] A. Peláiz-Barranco and P. Marin-Franch, *J. Appl. Phys.*, 2005, **97**, 034104.
- [S57] J. Yao, C. Xiong, L. Dong, C. Chen, Y. Lei, L. Chen, R. Li, Q. Zhu and X. Liu, *J. Mater. Chem.*, 2009, **19**, 2817.
- [S58] H. Tang, Y. Lin and H. A. Sodano, *Adv. Energy Mater.*, 2012, **2**, 469-476.
- [S59] H. Tang, Y. Lin, C. Andrews and H. A. Sodano, *Nanotechnology*, 2011, **22**, 015702.
- [S60] Y. J. Choi, M. J. Yoo, H. W. Kang, H. G. Lee, S. H. Han and S. Nahm, *J. Electroceram.*, 2012, **30**, 30-35.
- [S61] W. Nhuapeng and T. Tunkasiri, *J. Am. Ceram. Soc.*, 2004, **85**, 700-702.
- [S62] Y. Feng, H. Gong, Y. Xie, X. Wei, L. Yang and Z. Zhang, *J. Appl. Phys.*, 2015, **117**, 094104.
- [S63] L. Jylhä, J. Honkamo, H. Jantunen and A. Sihvola, *J. Appl. Phys.*, 2005, **97**, 104104.