Electronic Supplementary Information

A novel $BaTiO_3$-based lead-free ceramic capacitors featuring high energy storage density, high power density, and excellent stability

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Experimental section

Sample preparation

The 0.85BT-0.15BZS ceramic was prepared with $BaCO_3$ (99.0%), TiO_2 (99.8%), Bi_2O_3 (99.99%), ZnO (99.0 %) and SnO_2 (99.5%) by using conventional solid-state reaction. The raw materials were mixed and ball milled for 24h via ethanol. After drying, the mixture was calcined at 1000 ℃ in air for 2h. The calcined powder was re-milled, dried, and then pressed (120 MPa) into 13 mm diameter, pellets polyvinyl alcohol (PVA) as the binder was added. After burning PVA at 800 ℃ in air for 2h, sintering was carried out respectively at 1100, 1125, 1150, 1175, 1200, and 1225 ℃ for 2h. The sintered pellets were polished to 0.2 $\pm$ 0.02 mm and coated with silver paste (electrode area: 12.25 mm^2) to help measure the electrical properties.

Materials characterization

The density of those ceramic samples was measured by using the Archimedes method. The surface morphology and cross view of the ceramics were observed by using a scanning electron microscope (SEM; Hitachi, Tokyo, Japan). The cross-view morphology of the sample was investigated by a field emission scanning electron microscope (FESEM; Magellan400, FEI Company). The phase composition was evaluated by energy disperse spectroscopy (EDS, Oxford X-Max^N 80, Cambridge, UK) on FEI Magellan 400. The domain structure was investigated by piezoresponse force microscopy (Molecular Devices and Tools for Nanotechnology (NT-MDT) Co., Zelenograd, Russia) with out-of-plane. The crystal structure was examined by using X-ray diffraction (XRD, D/MAX-2550V; Rigaku, Tokyo, Japan) and Cu Kα radiation. The temperature and frequency dependence of the dielectric constant and dielectric loss (tanδ) were measured with a precision LCR meter (Novocontrol turnkey dielectric spectrometer, Concept 80, Germany). The capacitance-voltage and unipolar polarization-electric field (*P*-*E*) hysteresis loops were measured by using a commercial ferroelectric analyzer (TF Analyzer 2000, aixACCT, Aachen, Germany) at room temperature. The dielectric breakdown strength (BDS) measurement was performed by using a voltage-withstand test device at room temperature. The energy release

properties of ceramic capacitors were investigated via a charge-discharge platform with a specially-designed and high-speed capacitor discharge resistance, inductance, and capacitance load circuit (RLC)

Results and discussion section

Fig. S1 displays the SEM images of the cross-view of the 0.85BT-0.15BZS ceramic sintered at various temperatures. With the sintering temperature increasing from 1125 ℃ to 1150 ℃, there is a moderate increase in grain size, and the grain boundary seems to become increasingly more clear and tight. A further increase to 1175 ℃ in the sintering temperature leads to an inhomogeneous microstructure with different grain sizes. When the sintering temperature reaches to 1200 ℃, some of the grains increased abnormally because the ceramic sample appears to suffer a little over-sintering.

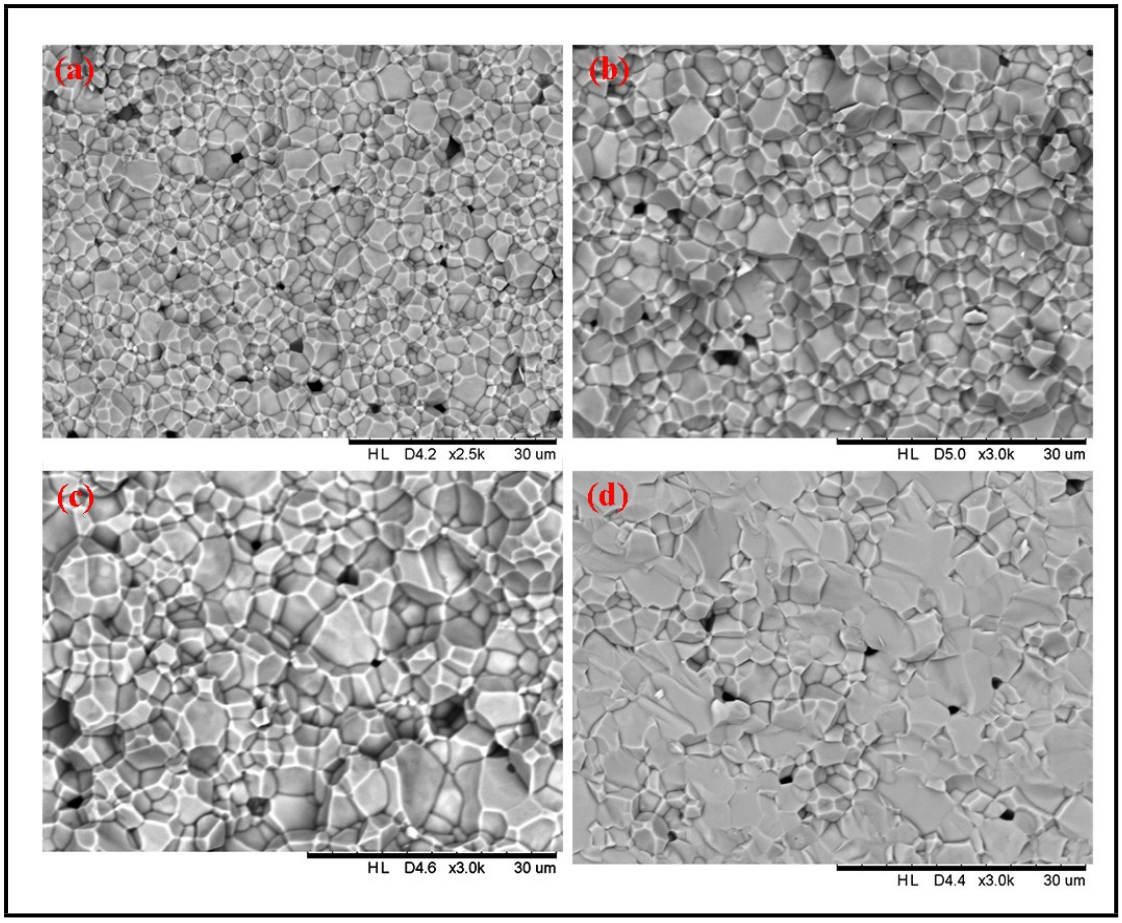

Fig. S1 SEM images of the cross-section of the 0.85BT-0.15BZS ceramics at different sintering temperatures: (a) 1125 ℃, (b) 1150 ℃, (c) 1175 ℃, (d) 1200 ℃.

The composition analysis of 0.85BT-0.15BZS ceramic was carried out and the EDS layered images and the spot scanning sites are shown in Fig. S2. It can be seen that the element of Ba, Ti, Bi, Zn, Sn, and O s are uniformly distributed in the 0.85BT-0.15BZS ceramics. Table 1 lists the atomic percentage of different elements in EDS area and spot scanning. All the elements are basically consistent with stoichiometric ration in the 0.85BT-0.15BZS ceramics.

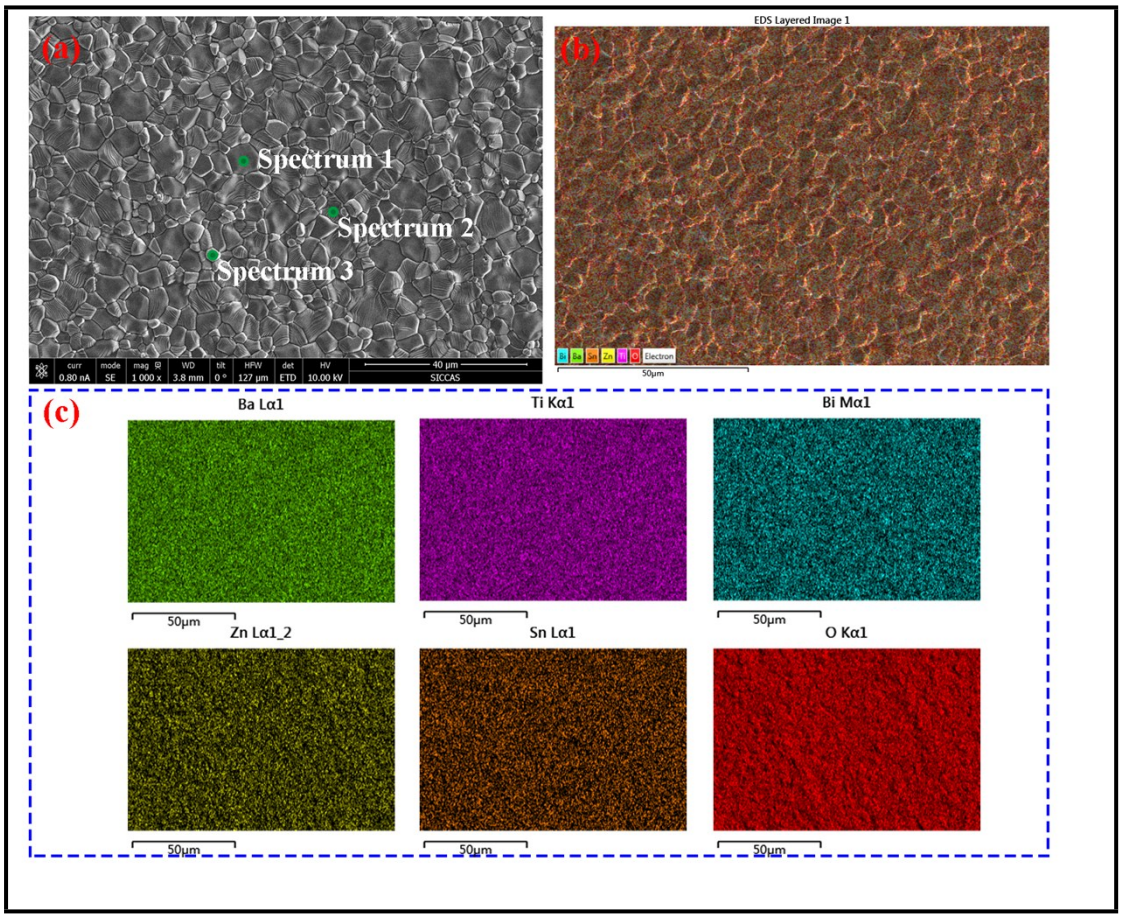

Fig. S2 The original surface (a) and EDS layered image (b, c) of the 0.85BT-0.15BZS ceramics (sintered at 1150 ℃ for 2 h in air condition)

Table. 1 The EDS area and spot scanning results (atomic percent, %) of the 0.85BT-0.15BZS from the Fig. S2

Element	Area scanning	Spectrum 1	Spectrum 2	Spectrum 3
O	59.91	59.78	59.99	59.95
Ba	17.34	17.81	17.13	17.07
Ti	16.79	16.63	16.64	17.11
Bi	2.93	2.87	3.07	2.95
Zn	1.49	1.41	1.61	1.46
Sn	1.50	1.50	1.55	1.45

Polished surface of topography and PFM image of 0.85BT-0.15BZS are displayed in Fig. S3(a) and (b), respectively. It is obviously that less dark and bright from distinct contrasts in Fig. S3(b), demonstrating that there is little trace of macro-domains for this component. However, a large numbers of nano-domains composed of PNRs can be observed in blue dotted line frame, which illustrates that 0.85BT-0.15BZS exhibits a typical characteristic of relaxor ferroelectric.

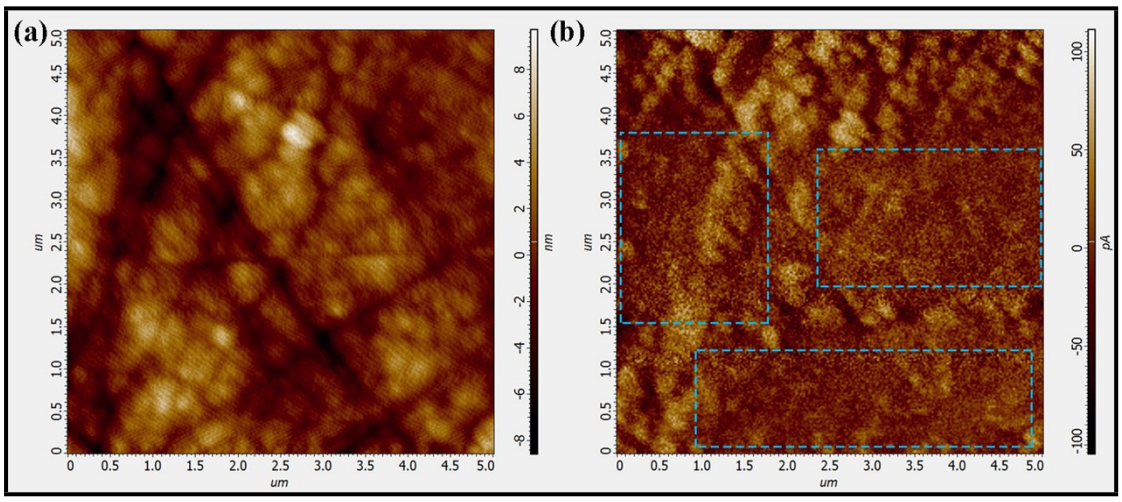

Fig. S3 (a) polished surface of topography of 0.85BT-0.15BZS ceramics. (b) Out-of-plane amplitude PFM image (5 × 5 μm^2) of 0.85BT-0.15BZS ceramics by applying a AC voltage of 10 V on the tip.

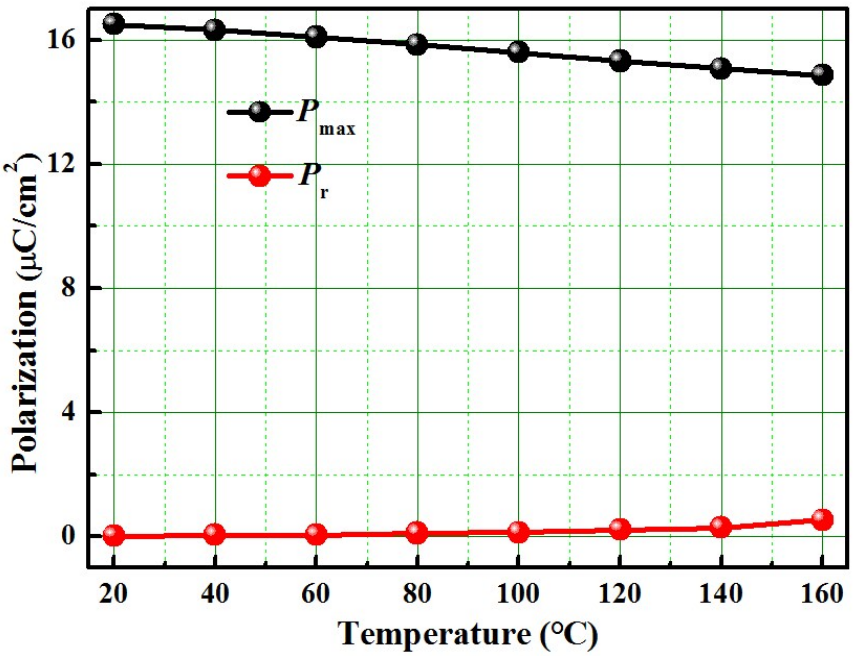

Fig. S4 The P_{max} and P_r of 0.85BT-0.15BZS ceramics at different temperatures under 150 kV/cm and 10 Hz.

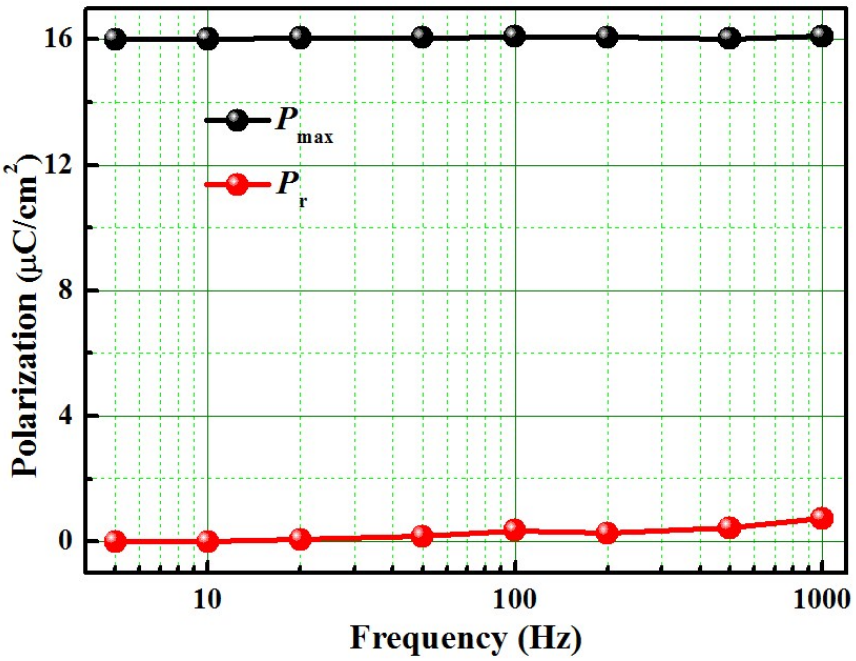

Fig. S5 The P_{max} and P_r of 0.85BT-0.15BZS ceramics at different frequencies under 150 kV/cm and at room temperature.

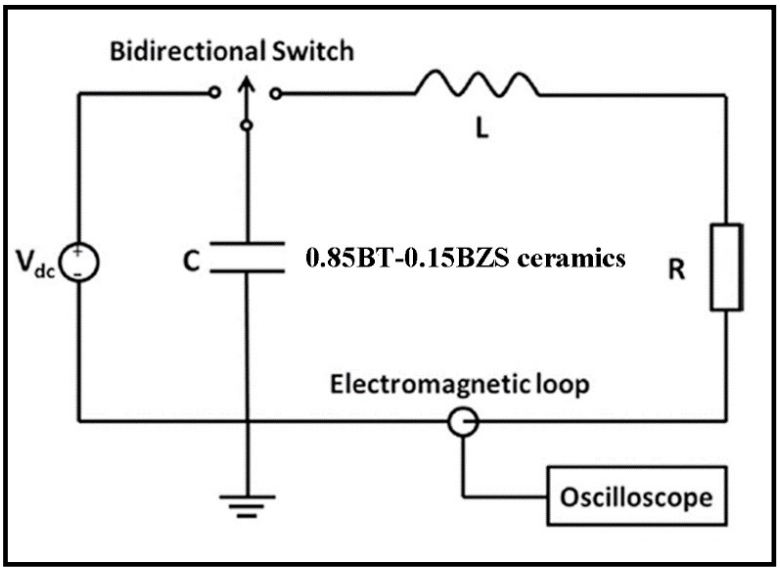

Fig. S6 Schematic diagram of the charge–discharge measuring system of 0.85BT-0.15BZS ceramics.

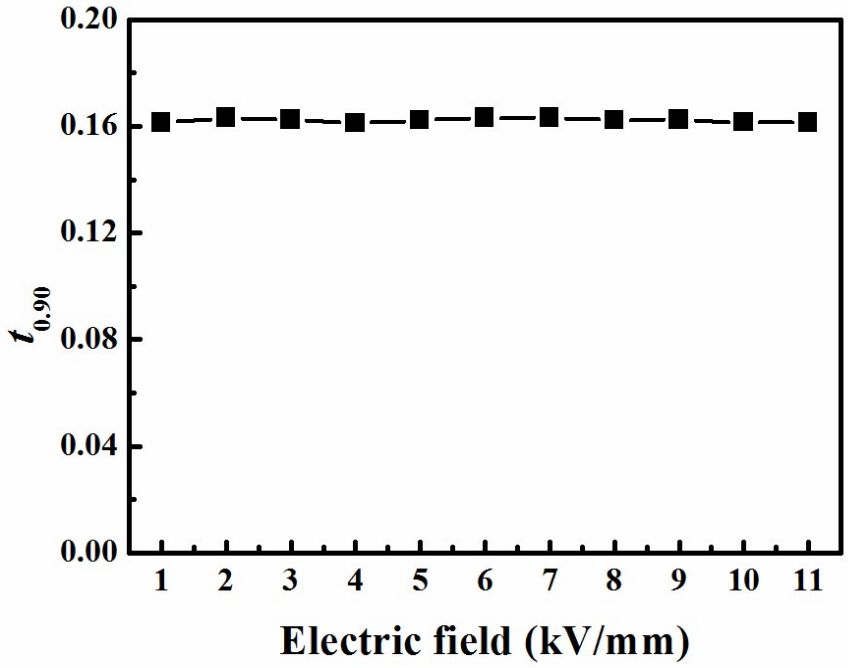

Fig. S7 Variation of $t_{0.90}$ as a function of the electric field of 0.85BT-0.15BZS ceramics at room temperature.

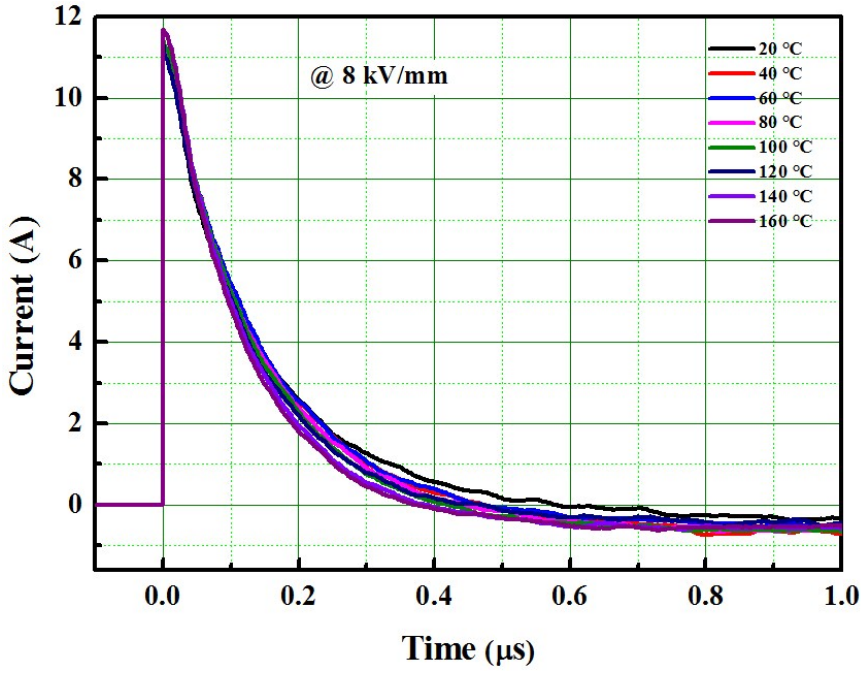

Fig. S8 Overdamped discharge waveforms of 0.85BT-0.15BZS ceramics over 20-160 ℃.

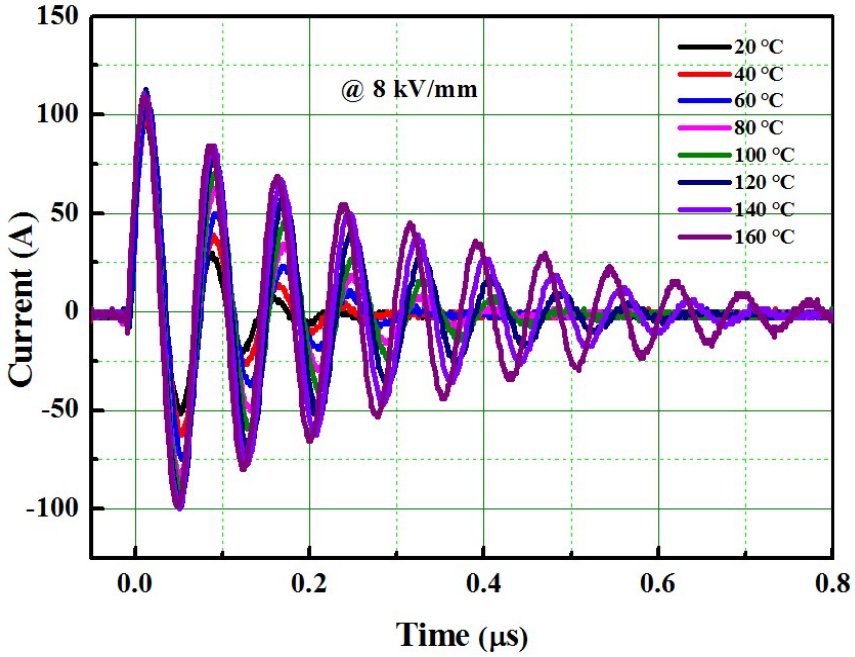

Fig. S9 Underdamped discharge waveforms of 0.85BT-0.15BZS ceramics over 20-160 ℃.

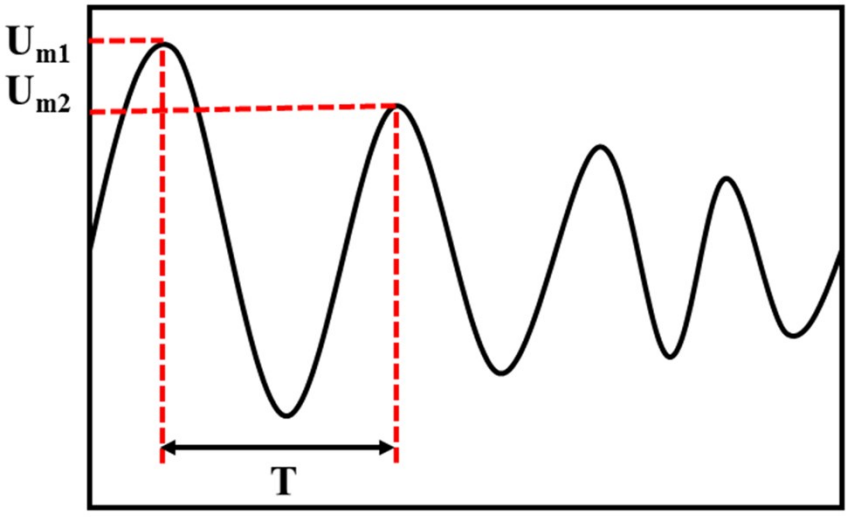

Fig. S10 Schematic definition of period time *T*.