Electronic Supplementary Information for PCCP article

High-performance colossal permittivity materials of (Nb+Er) co-doped TiO_2 for large capacitors and high-energy-density storage devices

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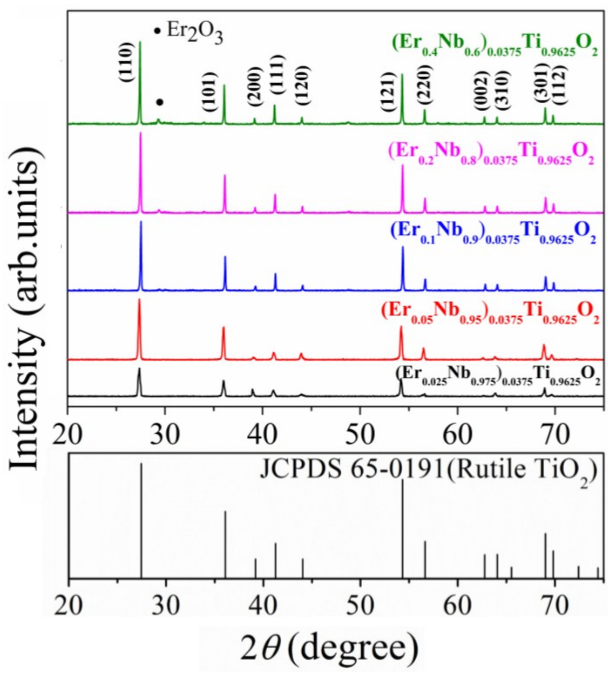

Fig. SI 1. XRD patterns of the $(Er_{0.025}Nb_{0.975})_{0.0375}Ti_{0.9625}O_2$, $(Er_{0.05}Nb_{0.95})_{0.0375}Ti_{0.9625}O_2$ and $(Er_{0.1}Nb_{0.9})_{0.0375}Ti_{0.9625}O_2$ sintered ceramics, $(Er_{0.2}Nb_{0.8})_{0.0375}Ti_{0.9625}O_2$ and $(Er_{0.4}Nb_{0.6})_{0.0375}Ti_{0.9625}O_2$ calcined powder.

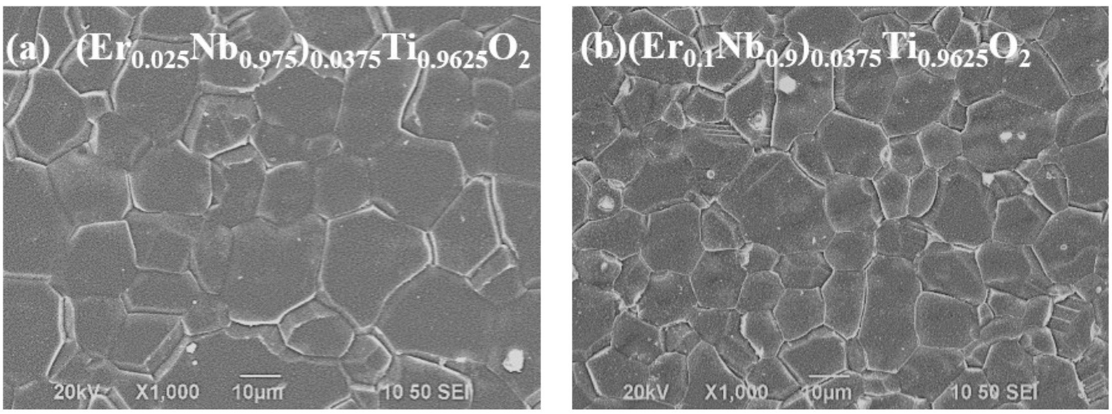

Fig. SI 2. Surface morphologies of the (Nb+Er) co-doepd TiO_2 ceramics without secondary phases at different doping contents: (a) $(Er_{0.025}Nb_{0.975})_{0.0375}Ti_{0.9625}O_2$ and (b) $(Er_{0.1}Nb_{0.9})_{0.0375}Ti_{0.9625}O_2$.

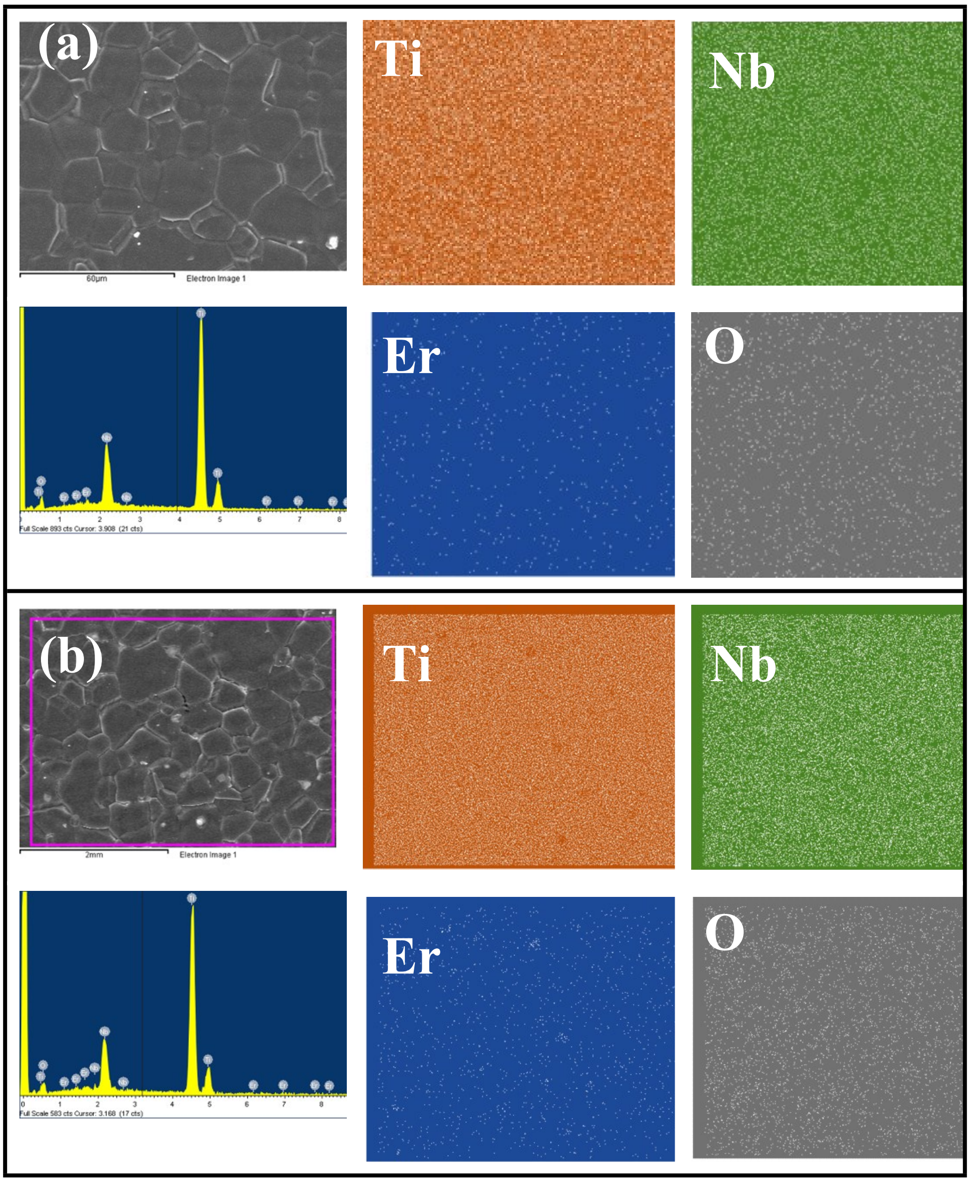

Fig. SI 3. Element mapping and EDS of the ceramics across entire section with (a) $(Er_{0.025}Nb_{0.975})_{0.0375}Ti_{0.9625}O_2$ and (b) $(Er_{0.1}Nb_{0.9})_{0.0375}Ti_{0.9625}O_2$.

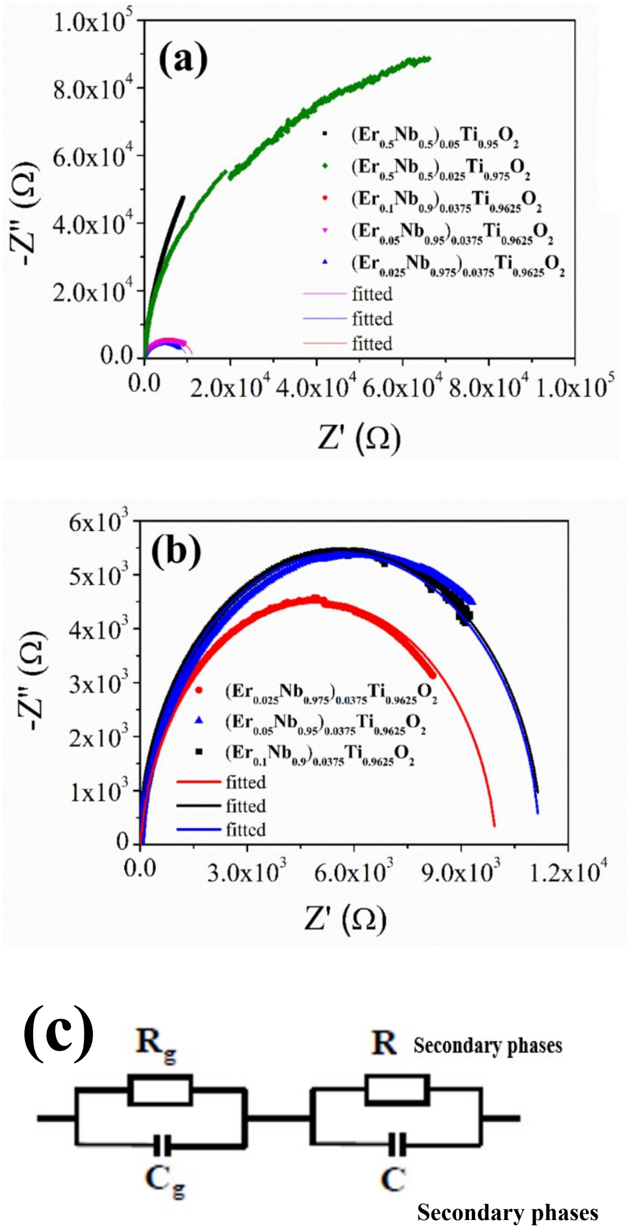

Fig. SI 4. (a) The complex impedance for the all various samples as a function of frequency at room temperature, (b) The magnifications of the complex impedance for the ceramics and (c) Two parallel RC equivalent circuits in series.

The complex impedance spectrum (Cole-Cole plot) technique is used for distinguishing the intrinsic (bulk) properties from the extrinsic contributions such as grain boundaries, surface layers, and electrode contacts.[1] This technique also provides the information about the resistive (real part) and reactive (imaginary part) components of the ceramics. Fig. SI 4. (a) presents the room temperature complex impedance for the various samples as a function of frequency. For the $(Er_yNb_{1-y})_{0.0375}Ti_{0.9625}O_2$ ceramics, y = 0.025, 0.05

and 0.1, the impedance spectra could be well fitted by a RC model. It consists of a bulk resistance and capacitance. It is observed that the samples showed single semicircle arc with centers lying below the real axis. The semicircle indicates the dominance of grain effect on the grain boundary and effect electrode.[2,3] For the ceramics of $(Er_{0.5}Nb_{0.5})_xTi_{0.95}O_2$, $x = 2.5\%$ and 5%, the impedance spectrum could not fitted by using one parallel RC model. With the combination of XDR patterns and SEM images results, these ceramics are assumed to be made up of parallel grains separated by secondary phases. This could be modeled by two parallel RC equivalent circuits in series as shown in Fig. SI 4. (c). Two arcs were observed for the $(Er_{0.5}Nb_{0.5})_xTi_{0.95}O_2$, $x = 2.5\%$ and 5% ceramics. Therefore, it can concluded that both intrinsic (electron-pinned defect-dipole) and extrinsic mechanisms contributed to the CP in the system[4], supporting our work.

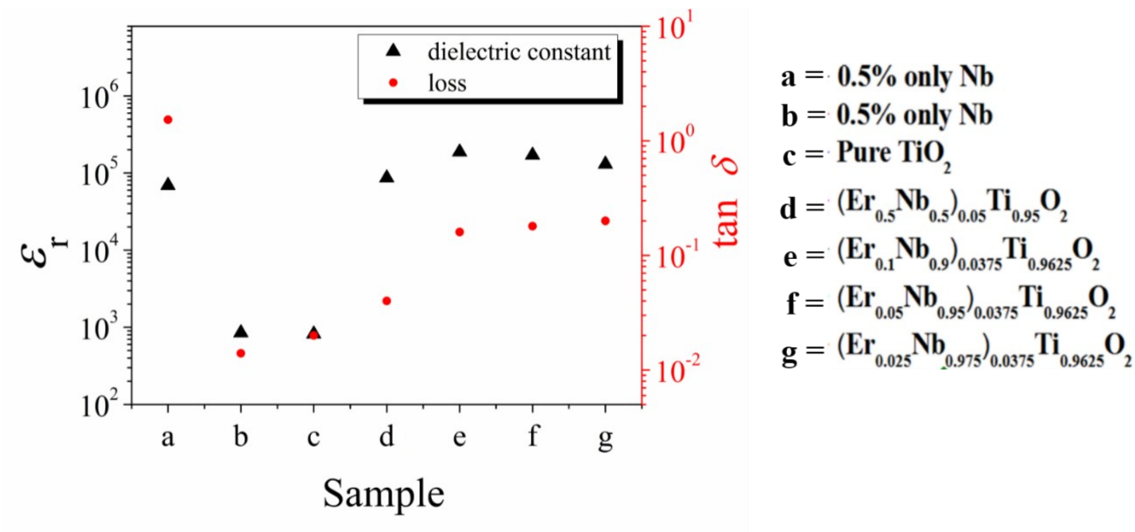

Fig. SI 5. Dielectric properties of various doping level of (Nb+Er) co-doped TiO_2 ceramics, measured at 1 kHz and room temperature.

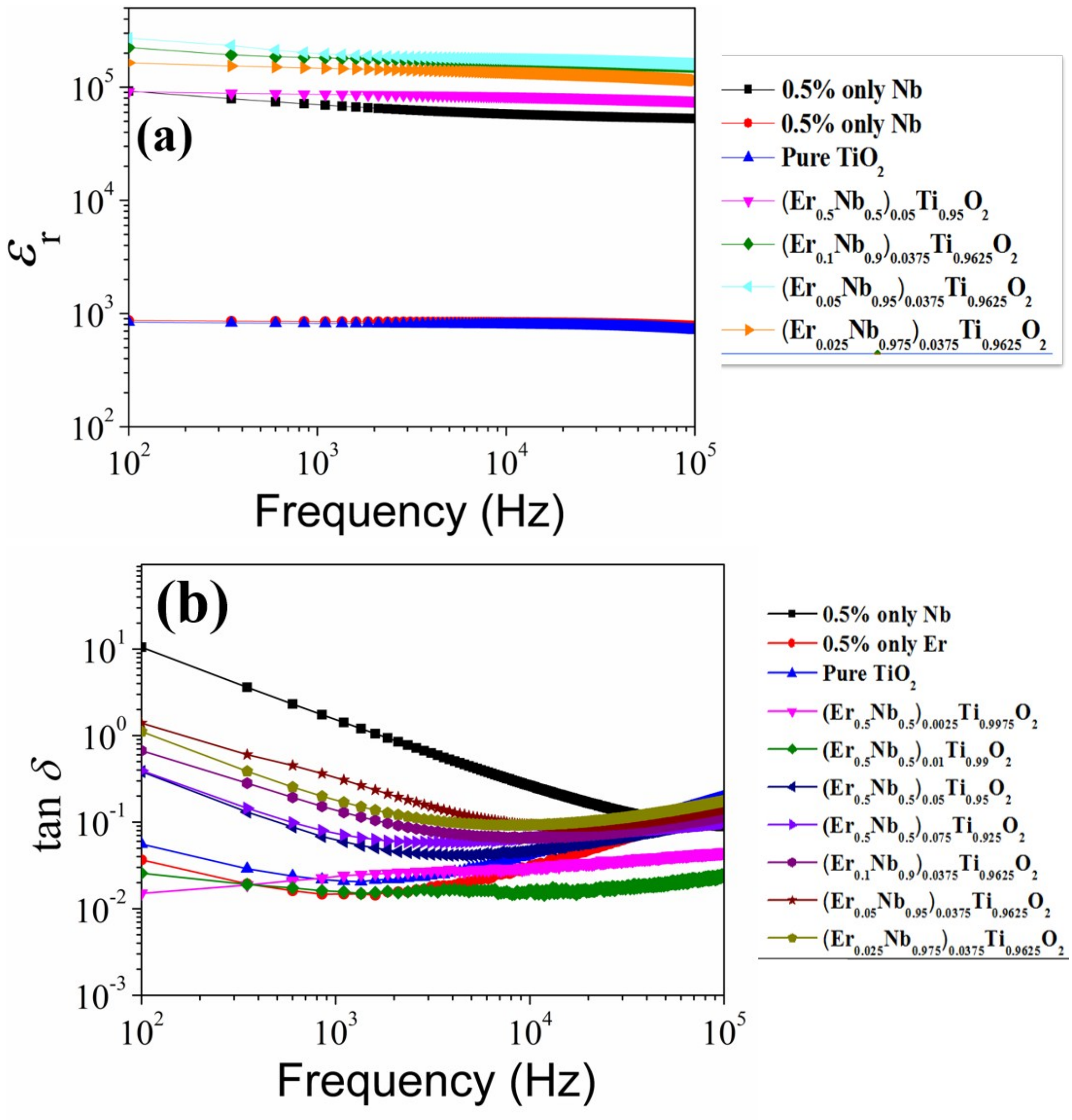

Fig. SI 6. Dielectric permittivity (a) and dielectric loss (b) of various doping level of (Nb+Er) co-doped TiO_2 ceramics in the frequency range of 10^2 to 10^5 Hz, measured at room temperature.

Fig. SI 5. presents the dielectric properties of various doping level of (Nb+Er) co-doped TiO_2 ceramics, measured at 1 kHz and room temperature. The results imply that the $(Er_yNb_{1-y})_{0.0375}Ti_{0.9625}O_2$ ceramics, y = 0.025, 0.05 and 0.1 ceramics, without secondary phases exhibited both higher CP and dielectric loss due to uneven ratio of Er^{3+} and Nb^{5+} ions. Besides, their dielectric loss were higher than those with secondary phases. We believe the extrinsic defects (secondary phases) play a significant role in determining the dielectric properties in this system. In this work, extrinsic defects may serve as an obstacle for inhibiting the inter-grain electron hopping. With intrinsic defect dipoles and extrinsic defects, the sufficiently low dielectric loss could be achieved. Fig. SI 6. compares the dielectric permittivity (a) and dielectric loss (b) of the various doping level of (Nb+Er) co-doped TiO_2 ceramics in the frequency range of 10^2 to 10^5 Hz, measured at room temperature. Therefore, it could be concluded that a combination of intrinsic and extrinsic defects for TiO_2 ceramics is needed for high performance CP behavior.

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