Electronic Supplementary Information

Nanoscale Mapping of Heterogeneity of the Polarization Reversal in Lead-Free Relaxor-Ferroelectric Ceramic Composites

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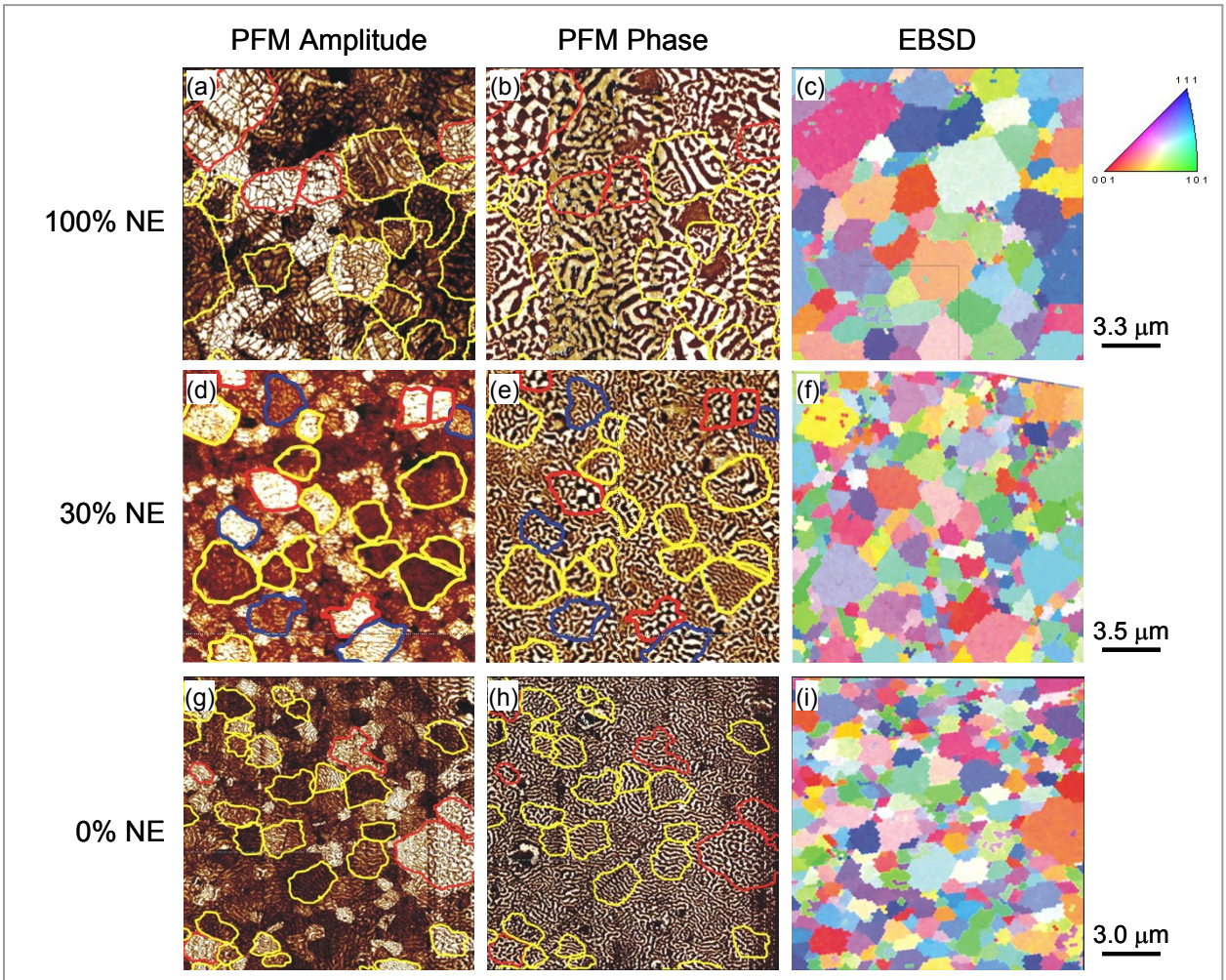

Figure S1. The PFM amplitude, PFM phase, and EBSD maps of the BNT-6BT-2KNN / BNT-7BT ceramic/ceramic composites with different content of nonergodic relaxor BNT-7BT: 100% (a-c), 30 % (d-f), and 0 % (g-i). Some grains are marked in PFM images to make comparison easier. For 100% NE sample, grains with <001> orientation show checkerboard patterns (some examples are marked red) that differ distinctly both in geometry and domain size from the labyrinth patterns of <001>-grains of 0%NE sample (also marked red). For the ER composition, we could not find the checkerboard pattern for any grain orientation (Figure S1 g-i). At the same time, the labyrinth and "distorted stripe" patterns can be assigned to <001>- and <111>-oriented grains, respectively. Obviously, this is the same domain pattern, but seen from different perspectives. In the composite samples (30% NE) grains with the orientation close to <001> show either checkerboard (red) or labyrinth (blue) patterns, proving coexistence of both NE and ER phases.

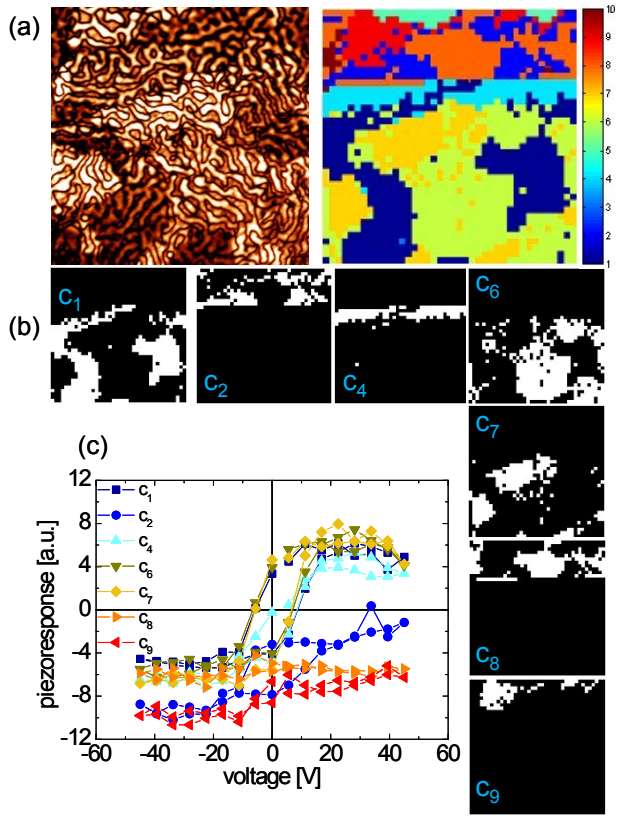

Figure S2. *Constituent diversity*: (a) The PFM image and the corresponding *k*-means clustering map for polarization switching for the ergodic relaxor BNT-6BT-2KNN sample. 10 clusters are considered. The points belonging to the same cluster have the same color in the cluster map; (b) The maps of clusters; (c) The local hysteresis loops of c_i clusters. Remarkably, for clusters c_8 and c_9 no hysteresis loops could be observed. In this case, the initially poled state was stable enough and resisted switching. At the same time, the clear localization of these clusters in the upper part of the scan may indicate that the observed behaviour is an artifact of measurements. E.g. an electric charge could accumulate on the tip at the beginning of the loops collection, which was dissipated later on. Such a charge might be origin of a permanent bias field that resulted in the strong polarization imprint.

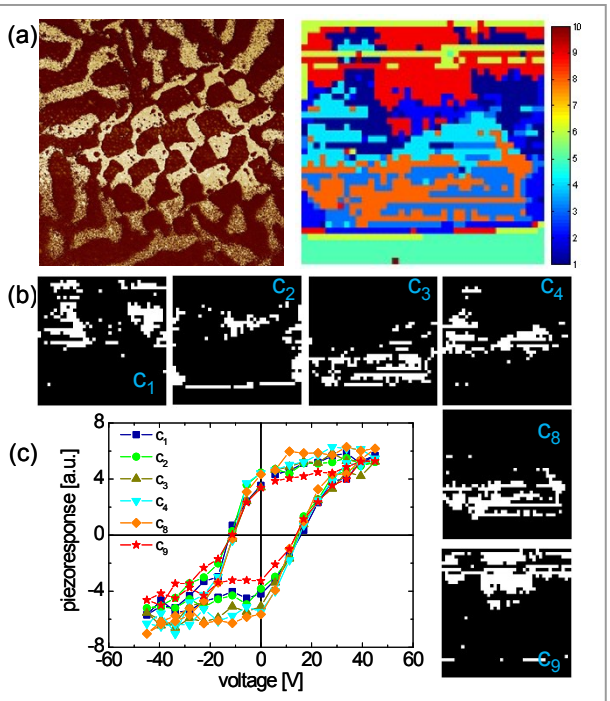

Figure S3. *Constituent diversity*: (a) The PFM image and the corresponding *k*-means clustering map for polarization switching for the nonergodic relaxor BNT-7BT sample. 10 clusters are considered. The points belonging to the same cluster have the same color in the cluster map; (b) The maps of some clusters; (c) The local hysteresis loops of c_i clusters.

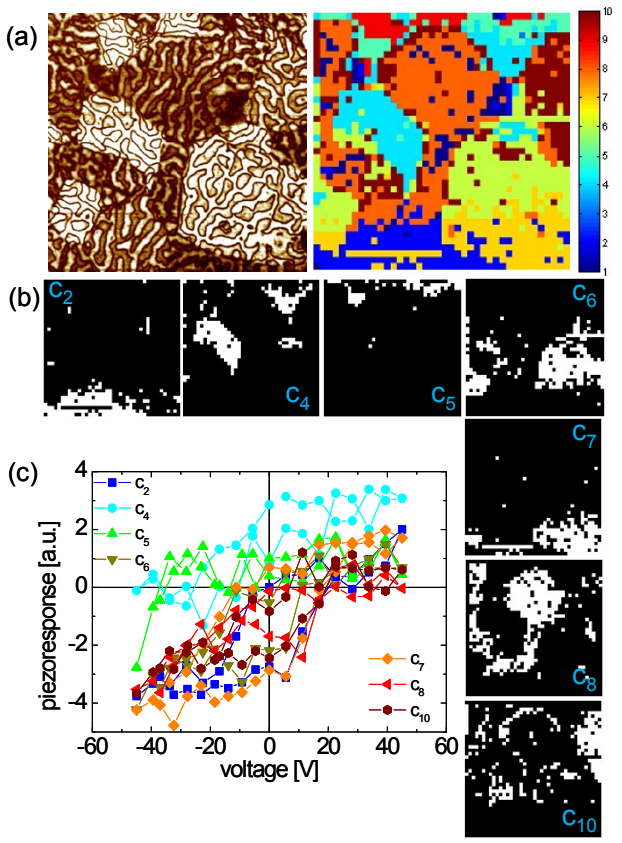

Figure S4. *Constituent diversity*: (a) The PFM image and the corresponding *k*-means clustering map for polarization switching for the composite ceramic with 10 vol% of BNT-7BT phase. 10 clusters are considered. The points belonging to the same cluster have the same color in the cluster map; (b) The maps of some clusters; (c) The local hysteresis loops of c_i clusters. For most of the clusters the representative loops have a strong negative offset. Only two clusters (c4 and c5) that correspond to two grains (on the left side and in the upper right corner of the PFM image) show a positive offset. However, no correlation between the polarity of the offset and domain pattern can be established.