BNT-based piezoelectric composite received intensive attentions as a promising candidate for replacing the environmentally hazardous Pb-based piezoelectric materials such as PZT. Bi$_{0.5}$(Na$_{1-x}$K$_x$)$_{0.5}$TiO$_3$–BiAlO$_3$ (BNKT-BA) ceramic is considered to be one of the replacements for such Bi-based piezoelectric materials due to its large strain value and high depolarization temperature ($T_d$). In spite of its improved piezoelectric properties, it still has low remanent polarization ($P_r$) and also requires large poling field to make phase transition from non-polar to polar phase. Recently, in order to complement these drawbacks, hard ferroelectric ceramic such as ferroelectric-Bi$_{0.5}$(Na$_{1-x}$K$_x$)$_{0.5}$TiO$_3$ (f-BNKT) was embedded in the BNKT-BA ceramics to decrease the poling field and increase $P_r$, however, there are still a few reports concerning the microscopic evolution during the phase change in terms of role of the ferroelectric phase on the piezoelectric properties of BNKT-BA ceramics.

In this study, we investigated the microstructure of BNKT-BA + f-BNKT and focused on the low electric field induced phase transitions. We used a modified in-situ electrical biasing transmission electron microscopy (TEM) stage for observing the phase change in real time. Before applying electric field, bright field (BF) images, centered-dark-field (CDF) images and selected area electron diffraction (SAED) patterns of the ceramics were systematically analyzed. From the superlattice spots of 1/2(000) and 1/2(00e) in the SAED patterns (FIG. 1 (b) and (c)), we notice the existence of the $R3c$ phase and the $P4bm$ phase which have anti-phase (a13-a13-a13) and in-phase (a00a00c) octahedral tilt symmetry, respectively. The morphology and distributions of these phases are also shown in the CDF images (FIG. 1 (d) and (e)). A notable point is that by adding the f-BNKT particles of 5–20 µm size, most of the BNKT-BA + f-BNKT grains forms in the type of mixture of ferroelectric $R3c$ (R phase) core region and relaxor-like ($R$+T phase) shell region. On the other hand, the grains of BNKT-BA ceramic without f-BNKT particles are comprised of typical relaxor type ($R$+T phase). The relaxor phases in the BNKT-BA ceramic never change by applying electric field up to 2kV/mm, whereas the domains are effectively realigned with the assistance of relaxor-like R+T phase even at lower than 1kV/mm, as shown in FIG. 2. Therefore, the inclusion of ferroelectric phases activates the domain propagation and alignment even at the low electric voltage, supposedly due to the formation of local polarized field at the interface between f-BNKT and relaxor BNKT-BA.

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Fig. 1: TEM micrographs of a core-shell grain in BNKT-BA+f-BNKT. (a) BF image of the grain with zone-axis. (b) and (c) SAED patterns of shell and core regions, respectively. (d) and (e) CDF images using $g=\frac{1}{2}(1-32)$ and $g=\frac{1}{2}(-3-1-1)$, respectively. (f) and (g) BF image and DF image using $g=\frac{1}{2}(031)$ in BNKT-BA grain with [013] zone-axis.

Fig. 2: TEM images of a core-shell grain under electric fields along [013] zone axis. (a) At 0kV/mm. The boundary between R-domain and T-domain is highlighted by yellow dotted lines. (b) At 1kV/mm. (c) At 2kV/mm. (d) After poling.
(e), (f) SADE patterns from region R and T, respectively.