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Supplementary information

Effect of poling on nanodomains and nanoscale structure in A-site disordered lead-free piezoelectric Na_{0.5}Bi_{0.5}TiO₃-BaTiO₃

Figure S1 shows the SEM micrograph of the NBT-BT sample. The average grain size in this system was found to be 2μ m as calculated using line intercept method. One can clearly see highly dense ceramic body on NBT-BT. Figure S2 shows XRD spectra recorded at RT for poled and un-poled NBT-BT samples. The absence of any secondary phase peak shows high quality of ceramic sample of NBT-BT. The change in the intensity of peaks and emergence of new peaks clearly shows structural transformation under *E*-field.



Figure S1: SEM micrograph of the sintered NBT-BT sample



Figure S2: XRD spectra recorded at RT for poled and unpoled NBT-BT samples using Cuka radiation.

Figure S3 shows the SEM micrographs of PZT samples, which was used to demonstrate the difference of variation in poling field on the d_{33} value of PZT and NBT-BT. The grain size of PZT sample was about 1.0 µm. The micrographs clearly show highly dense ceramic body of PZT. The synthesis of 5 mol% Nb doped PbZr_{0.52}Ti_{0.48}O₃ (PZT) piezoelectric ceramics was performed using conventional solid state reaction method. For this, stoichiometric amounts of PbO, ZrO₂, TiO₂ and Nb₂O₅ was ball-milled under ethanol for 24 h. The resulting products were kept for drying at 80°C for 6 h followed by calcination. The calcined powder was again ball-milled for 48 h followed by drying and sieving. These poweders were pressed into pellets. The cold isostatic pressing (CIP) technique was used to increse green densitiy of these pellets. These pellets then sintered at high temperature 1200-1300°C for 4 h for achiveing highly dense ceramic

body of PZT. In order to confirm the formation of pure phase, XRD spectra was recorded at room temperature for PZT (Figure S4). For the electrical measurements, silver electrodes were fired at 650°C on the polished ceramic pellets of PZT in the same fashion as that of NBT-BT. Figure- S5 shows d_{33} versus poling field plots for NBT-BT and PZT. From this plot, one can clearly see the difference in the poling behavior and resultant d_{33} for NBT-BT and PZT. We chose PZT (due to its commercial importance in the piezoelectric industry) to demonstrate the difference in poling behavior with NBT-BT.



Figure S3 SEM micrographs of 5 mol % Nb doped PZT.



Figure S4: XRD spectra recorded at RT for PZT ceramic samples using Cukα radiation.



Figure-S5: Comparative variation in the longitudinal piezoelectric response (d_{33}) with applied *E*-field during the poling process for NBT-BT and soft PZT.

In order to investigate local structural changes due to poling, HR-TEM images from [111] and [110] zone axis were recorded (Fig. S6 and S7). The absence of satellite peaks clearly suggests reduction in the degree of disorder in poled specimen.



Figure S6: HR-TEM image of poled NBT-BT with electron beam incident from [111].

Figure S7: HR-TEM image of poled NBT-BT with electron beam incident from [110].

The impedance cole-cole plots for poled and unpoled samples have been plotted in Fig. S8. Due to high resistivity, only a small arc of semi-circle was visible (almost parallel to the imaginary impedance axis) suggesting very high resistance. However, a more pronounced arc of the

semicircle was seen at 300°C for both the poled and unpoled NBT-BT samples due to increased conductivity at higher temperatures (300°C). Please note the similarity of this arc in both poled and un-poled samples. In order to capture full cole-cole plots in these systems we need a delicate combination of resistance and frequency range measurements at room temperature. At high temperature (above 300°C), we expected a pronounced semicircle in the impedance cole-cole plots. However, we were interested in understanding the differences in polar ordering below the depoling temperature (T_{d} ~ 125°C) in poled and un-poled NBT-BT. Above T_{d} , both the materials have similar physical properties.

Figure S8: Cole-cole plots at various temperatures for (a) unpoled and (b) poled NBT-BT samples. The inset of Fig. 8(a) and (b) shows the col-cole plots at 300°C. Please note more pronounced cole-cole plots at 300°C for poled and unpoled samples.