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Supplementary Materials

Effect of Oxygen Annealing Atmosphere on Structural, Electrical and Energy Storage Properties of $Bi_{0.5}Na_{0.5}TiO_3$ Polycrystalline Thin Film

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1. Microstructural analysis

Scanning microscopy (SEM) micrographs of thin BNT films annealed at 600 °C under different atmospheres are shown in Figure S1. It is worth noting that BNT films annealed under oxygen, exhibits a relatively dense grained structure without electron porosity and cracks. In addition, grains seems to be uniformly distributed (Figure.S1a). However, the films annealed under N_2 (BNT-N_2) (Figure.S1b) show sponge like microstructure similarly to what is reported by Yang et al.[1] for $Na_{0.51}Bi_{0.50}(Ti_{0.96}W_{0.01}Ni_{0.03})O_3$ thin films. The authors showed that the microstructure is governed by Na nonstoichiometry. Such sponge microstructure is observed for the composition with high oxygen vacancy concentration and larger grain size. Finally, for the films annealed under Argon (BNT-Ar) (Figure.S1c), the microstructure consists of equiaxed grains with some scattered pores but are rather dense and smooth across the full sample, in good agreement with typical microstructure reported in the literature for BNT thin films prepared by CSD [2]. A typical cross-section of the films annealed under O_2 (BNT-O_2), is presented in Figure S1d. It evidences a uniform thickness of about 475.6 nm (note that no significant influence of the annealing atmosphere on the films thickness was observed).

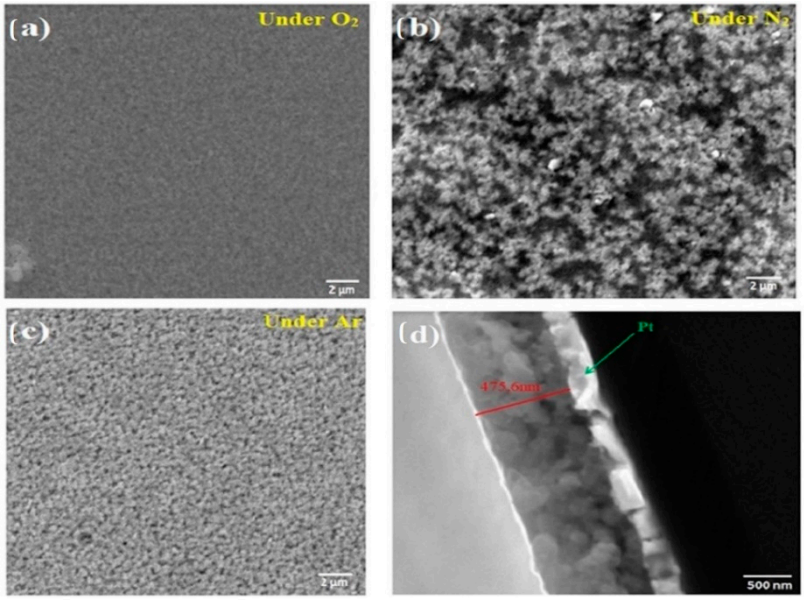

Figure S1. SEM images showing the microstructure of BNT thin films annealed at 600 °C under different atmospheres (a) O_2, (b) N_2 and (c) Ar, (d) Example of cross-sectional image of the BNT thin film annealed under O_2.

Figure S2 presents the EDX spectra in compositional distribution for the investigated BNT films. As expected, characteristics of starting elements, namely Bi, Na, Ti and O, are detected. A close look to the obtained atomic weight reveals that the BNT films annealed under O_2 (BNT-O_2; Figure S2a) or Ar (BNT-Ar; Figure S2b) atmosphere show deficiency of Na atoms compared to the samples annealed under N2 (BNT-N_2; Figure S2c).

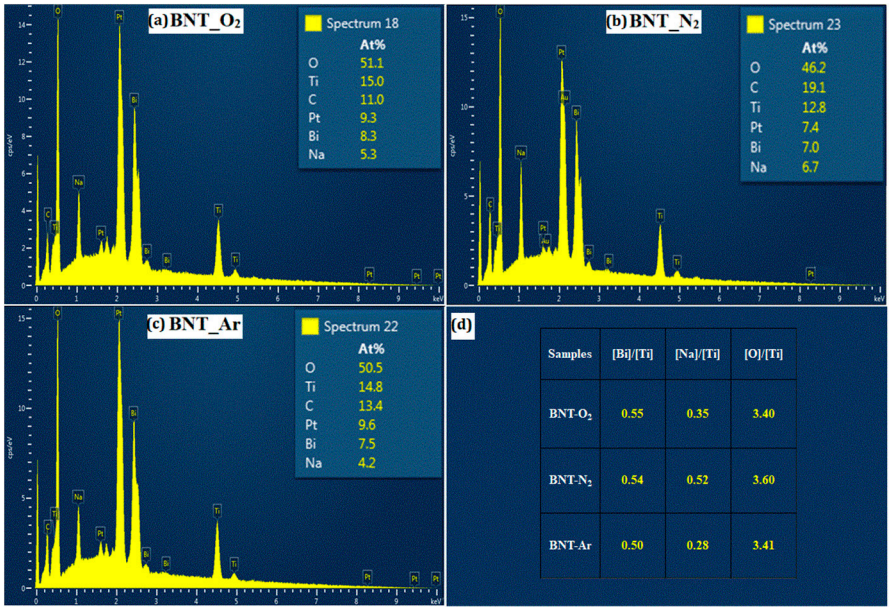

Figure S2. EDX spectra with elemental composition of BNT thin films annealed under O2, N2, and Ar atmospheres

The surface topography and roughness investigated by AFM provide more insight into the understanding of the microstructure. The topography of the film surfaces obtained in contact mode AFM is shown in Figure S3. The images were recorded on the 10 × 10 μm^2 scan regions. A fine-grained structure is observed for all samples which are essentially smooth. Nevertheless, if we look more closely the 2D and 3D AFM images, we can notice that the grains are larger for the films treated under N_2 and Ar. This result is confirmed by the root mean square (RMS) roughness whose value around 1.5 nm for the film treated under O_2 atmosphere, increases by a factor of two for the film treated under N_2 (Rms ~3.9 nm) or under Ar (Rms ~2.9 nm). This clearly demonstrates that the microstructure is affected by the nature of the gas atmosphere.

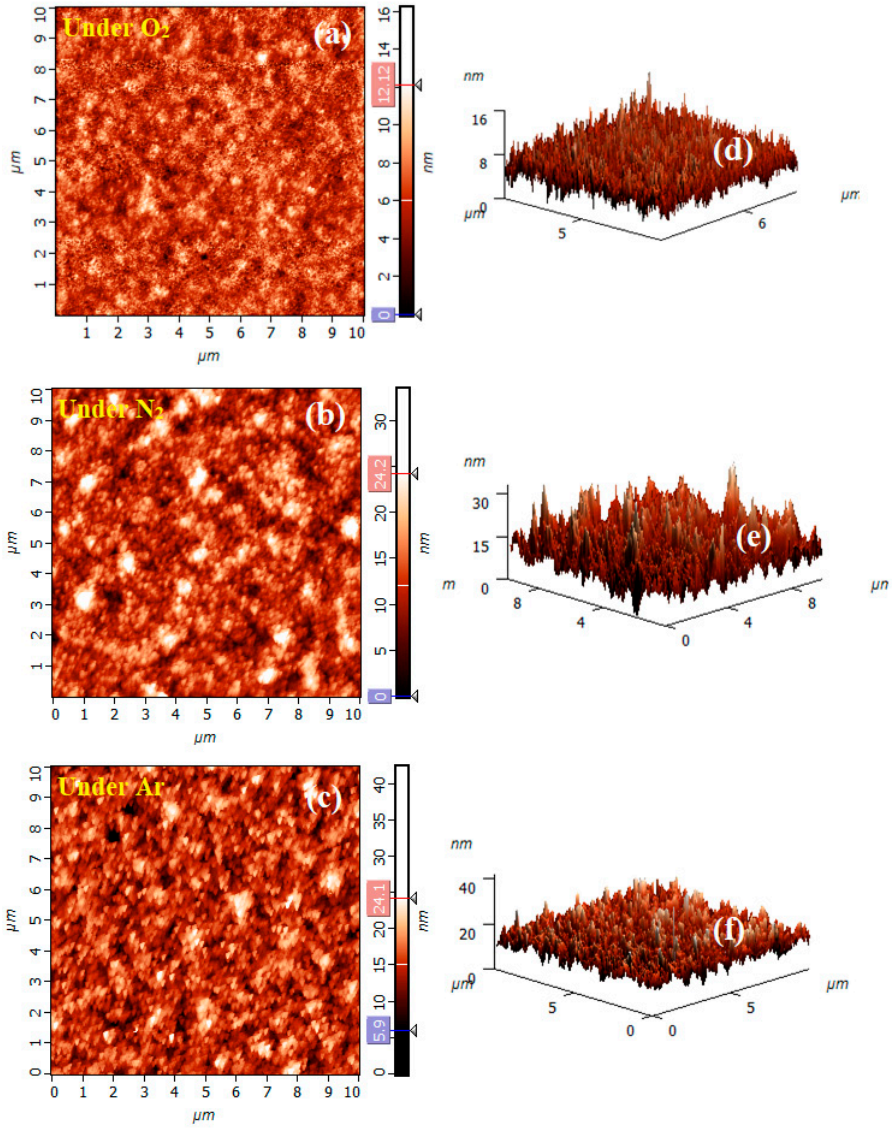

Figure S3. (a, b and c) AFM micrographs of the BNT thin films deposited by the Sol gel method on a Pt/SiN substrate under the atmospheres of oxygen, nitrogen and argon, respectively; and (d, e and f) the corresponding 3D AFM images, respectively.

2. Structural investigations

The XRD patterns of the investigated samples are shown in Figure S4. The grazing incidence mode (GI) was used to eliminate the substrate contribution. Both films annealed under N_2 and Ar showed the presence of peaks of BNT perovskite in addition to the peaks of the secondary phase. The obtained diffraction peaks of Au are coming from the top electrodes déposited for electrical measurents. Only the film annealed under O_2 leads to a pure BNT perovskite.

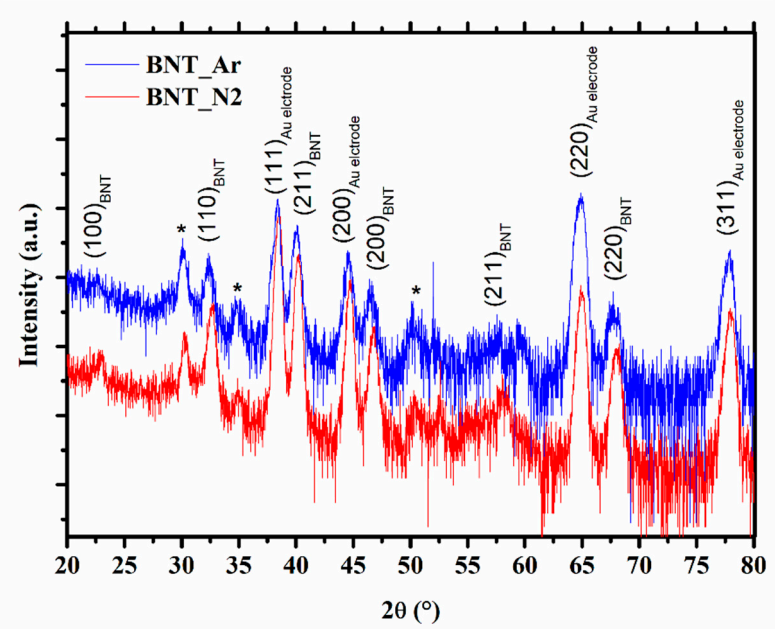

Figure S4. Room-temperature x-ray diffractogram of BNT thin films annealed under N_2 and Ar atmospheres.

Raman spectroscopy is used in the present work as a powerful tool to get complementary information about the structural changes, which are not accessible by XRD technique. The room temperature spectra of the investigated films are presented in Figure S5, together with the Raman spectrum of a BNT ceramic given for comparison.

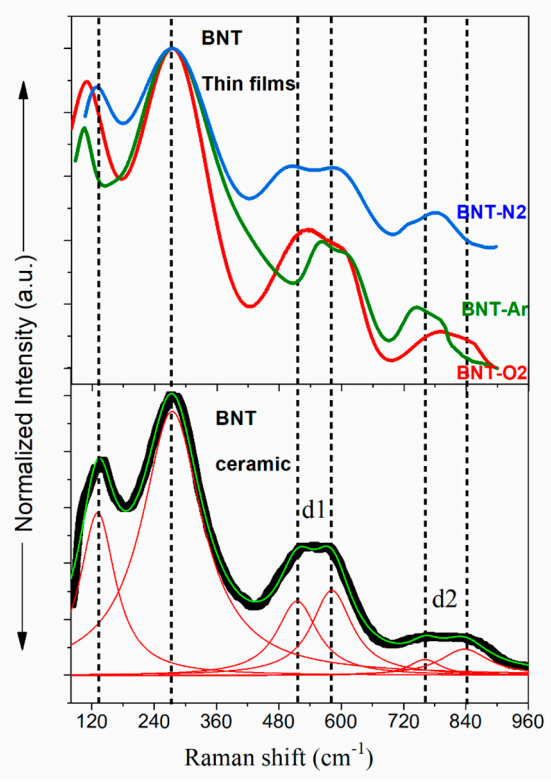

Figure S5. Comparison of the room temperature Raman spectra of the BNT thin films annealed under different atmosphere. The spectrum of a BNT ceramic is given as reference.

The comparison of the Raman spectra presented in the figure 5 shows that for all samples no change in position is detected for the intense band assigned to the Ti-O vibration at 275 cm^{-1} as in the bulk ceramic. However, the lower mode corresponding to the Na-O vibration exhibits a downward shift for both BNT-O_2 and BNT-Ar films. The shift of this mode towards lower frequencies could be attributed to the Na+ deficiency.

3. Ferroelectric properties

Figure S6 shows the ferroelectric properties at room temperature for both BNT-N_2 and BNT-Ar samples. Only, a leaky hysteresis loops are obtained for both BNT-N2 and BNT-Ar.

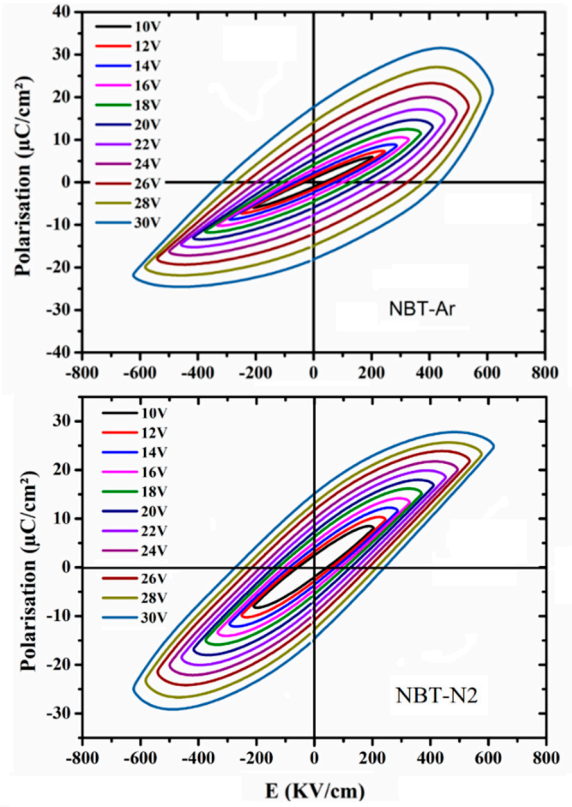

Figure S6. P-E hysteresis loop of BNT thin films prepared under Ar and N_2 atmosphere, respectively.

References

1. Yang CH, Yao Q, Qian J, et al (2018) Growth, microstructure, energy–storage and dielectric performances of chemical–solution NBT–based thin films: Effect of sodium nonstoichimometry. Ceramics International 44:9152–9158. https://doi.org/10.1016/j.ceramint.2018.02.123

2. Zannen M, Belhadi J, Benyoussef M, et al (2019) Electrostatic energy storage in antiferroelectric like perovskite. Superlattices and Microstructures 127:43–48. https://doi.org/10.1016/j.spmi.2018.03.041