## **Supporting Information**

# High Spatial Resolution Structure of (K,Na)NbO<sub>3</sub> Lead-Free Ferroelectric domains

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### F.Rubio-Marcos et al. Supporting Info 1



Supporting Info 1. XRD patterns of the sintered sample at 1080°C for 4 h. The inset shows a detail

of the XRD diffraction pattern in the 2O range 44° to 47° and 50° to 54° of the KNN ceramic.

(Supporting Info 1) Table 1. Unit-cell parameters of  $(K_{0.5}Na_{0.5})NbO_3$  ceramics at room temperature.

Unit-cell parameters					
	a [Å]	<b>b</b> [Å]	<b>c</b> [Å]	<b>β</b> [°]	Volume [Å <sup>3</sup> ]
(K <sub>0.5</sub> Na <sub>0.5</sub> )NbO <sub>3</sub>	$4.01095 \pm 0.00015$	$3.94672 \pm 0.00008$	$4.00034 \pm 0.00012$	$90.30805 \pm 0.0016$	$\textbf{63.373} \pm \textbf{0.003}$

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Details experimental

*Structural Characterization: The* crystalline structure was studied by X-ray diffraction (XRD, Bruker advanced D-8 diffractometer) on powder obtained by milling of the sintered ceramics. The lattice parameters were refined by a global simulation of the full diagram (pattern matching, *fullprof* program).

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#### F.Rubio-Marcos et al. Supporting Info 2

The scanning electron microscopy, SEM, micrograph of **Figure S2**a shows a typical KNN morphology. It can be observed that the sintered sample is composed by grains with platelet morphology that correspond to nearly cuboidal particles. It is possible to observe that the crystals have grown considerably. The pictures also revealed an average grain size of 63  $\mu$ m.

In order to analyze the domain structure, several SEM images were taken over the chemically etched sample. Figure S2b shows the complex structure of domains in KNN piezoelectric ceramics for the sintered and chemically etched sample. From this image the domain structure was elucidated, 90° and 180° ferroelectric domains were developed.



(**Supporting Info 2**) Scanning electron micrographs of the sintered sample at 1080°C for 4h, (a) before and (b) after of the chemical etch. The sintered sample was chemically etched in HF (48 vol. %) at room temperature for five minutes with no additional treatment.

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#### Details experimental

*Microstructural Characterization:* The sample was analyzed without any metal coating in a scanning electron microscopy (Leica STEREOSCAN 440), the current and voltage conditions were set at 0.5 nA and 20 kV, respectively. The work distance was established at 13 mm. The average grain size was determined from the SEM pictures using an image processing and analysis software (ImageJ). The surface of each grain was measured and its size was calculated in terms of equivalent-diameter for circular geometry; the average grain size (two–dimensional grain diameter) and size distribution were determined from the measurement of 400–600 grains per sample.