

Supporting Information

Revealing the Role of Cationic Displacement in Potassium-Sodium Niobate Lead-free Piezoceramics by adding W^{6+} ions

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L. Ramajo et al. Supporting Info 1

The average Raman spectra of the secondary phase is shown in **Figure S1**, which can be indexed on the basis of a phase mixture constituted by a majority of KNN-based phase and a minority of secondary phase. The localization of the secondary phase can be observed in the **Fig. 2(c-f)** of the main manuscript, which is signaled as blue regions. As alluded earlier in the main manuscript, this secondary phase was not observed by corresponding X-ray diffraction pattern, especially for the ceramics with $x \leq 0.01$.

In order to determine the isolate Raman spectrum of the secondary phase, additional analyses were performed. This spectrum was determined by using Witec Control Plus Software. So, the discrimination of the secondary phase was calculated from Average Raman spectra of $KNL-(NTS)_{1-x}W_{5x/6}$ ceramics associated with the secondary phase. Then, the spectra are fitted to the sum of two spectra: the first one is associated with the matrix Raman spectrum, as it is well known for the piezoelectric KNN-based perovskite systems; and the second one is ascribed to the secondary phase with TTB structure (bottom of the **Fig. S1**). In previous studies concerning the KNL-NTS compounds, we have demonstrated that the secondary phase could be assigned either to $K_3LiNb_6O_{17}$ (KLN) (PDF#36-0533) or $K_6Nb_{10.88}O_{30}$ (PDF#87-1856), both with tetragonal tungsten-bronze type structure (TTB) [1-3].

Therefore, we think that it is also worth to notice other characteristics revealed by the CRM imaging since it has been possible to detect the presence of a secondary phase previously was not observed by XRD.

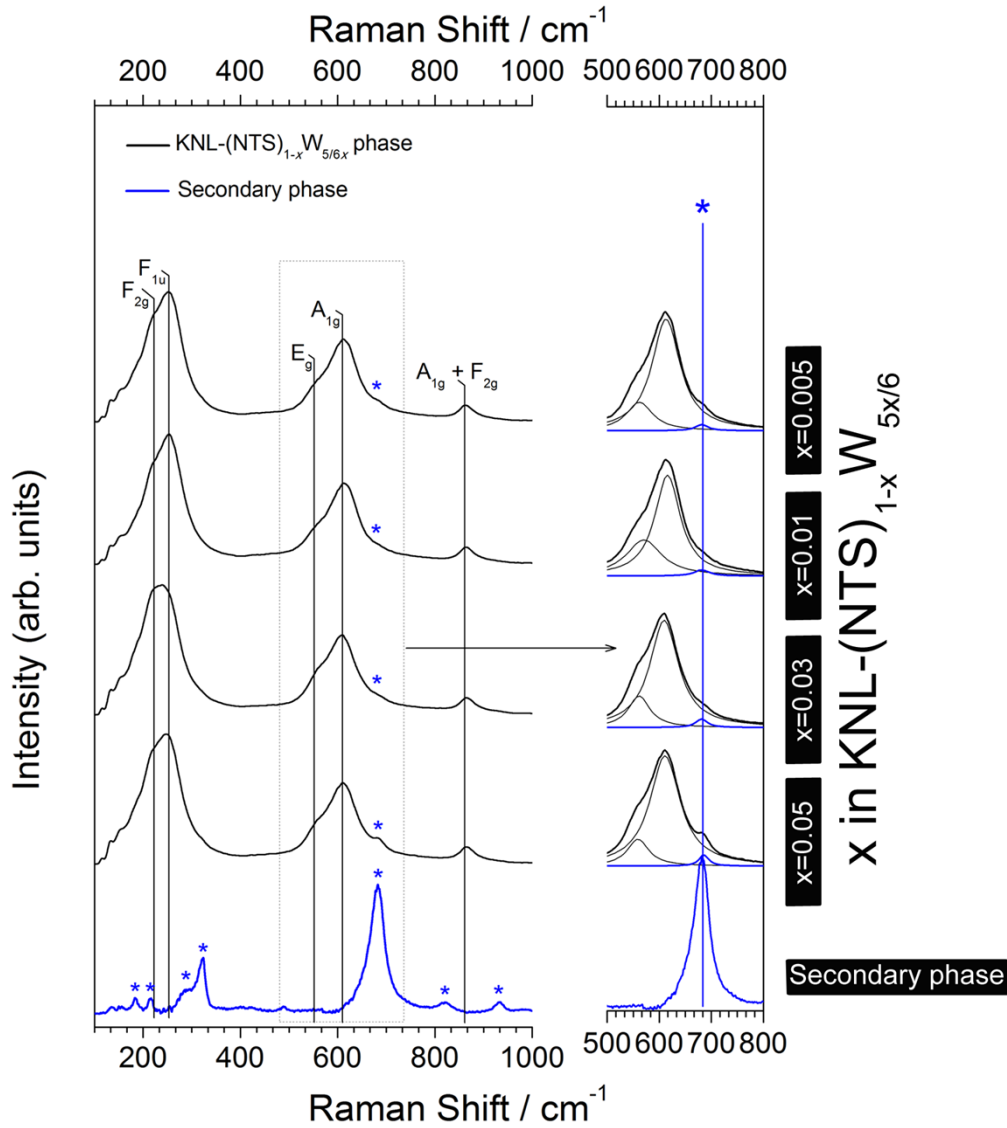


Figure. S1. Characterization of the secondary phase observed in the $\text{KNL}-(\text{NTS})_{1-x}\text{W}_{5x/6}$ system sintered at $1125\text{ }^\circ\text{C}$ through confocal Raman spectroscopy: Experimental Raman spectra corresponding to a KNN-based matrix and a minority secondary phase, which is signalled with a blue asterisk (*). These spectra are fitted to the sum of two spectra, which can be discriminated by using Witec Control Plus Software. Calculated Raman spectra of the MATRIX and of the secondary phase (in bottom). In addition, the isolate Raman spectrum of the secondary phase has been magnified 10 times due to its low Raman intensity compared to the Raman spectrum of the KNN-based ceramic (MATRIX). The inserts of the Fig. 1S show magnified Raman spectra in the frequency range between 500 to 800 cm^{-1} .

References

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