Supplementary information

Figure S1 shows a schematic of the polishing process of as-sintered conventional and FLASH ceramics in a) and the respective surface of analysis in b). Approximately one third to one half of the ceramic thickness was removed (stripes in the figure) by polishing with SiC paper. The final polishing was performed with a P4000 paper, equivalent to a grain size of ≈ 5 μm. After polishing, specimens were washed in ethanol under sonication. The dried ceramics were then analysed by X-ray diffraction and Raman spectroscopy using single spot and imaging mode.

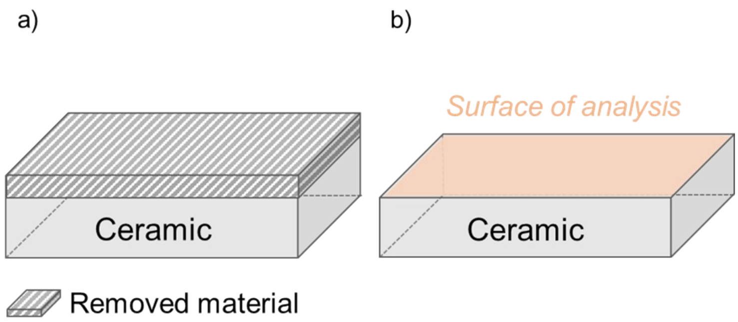


Figure S1 – Schematic representation of a) polishing process with indication of removed material and b) the revealed surface for X-ray diffraction, SEM and Raman spectroscopy analysis. The polishing step allowed the central part of the ceramics (core) to be simultaneously revealed with their surface.

More details on the microstructure of these ceramics can be found in reference 6 and supplementary information Figure S2.

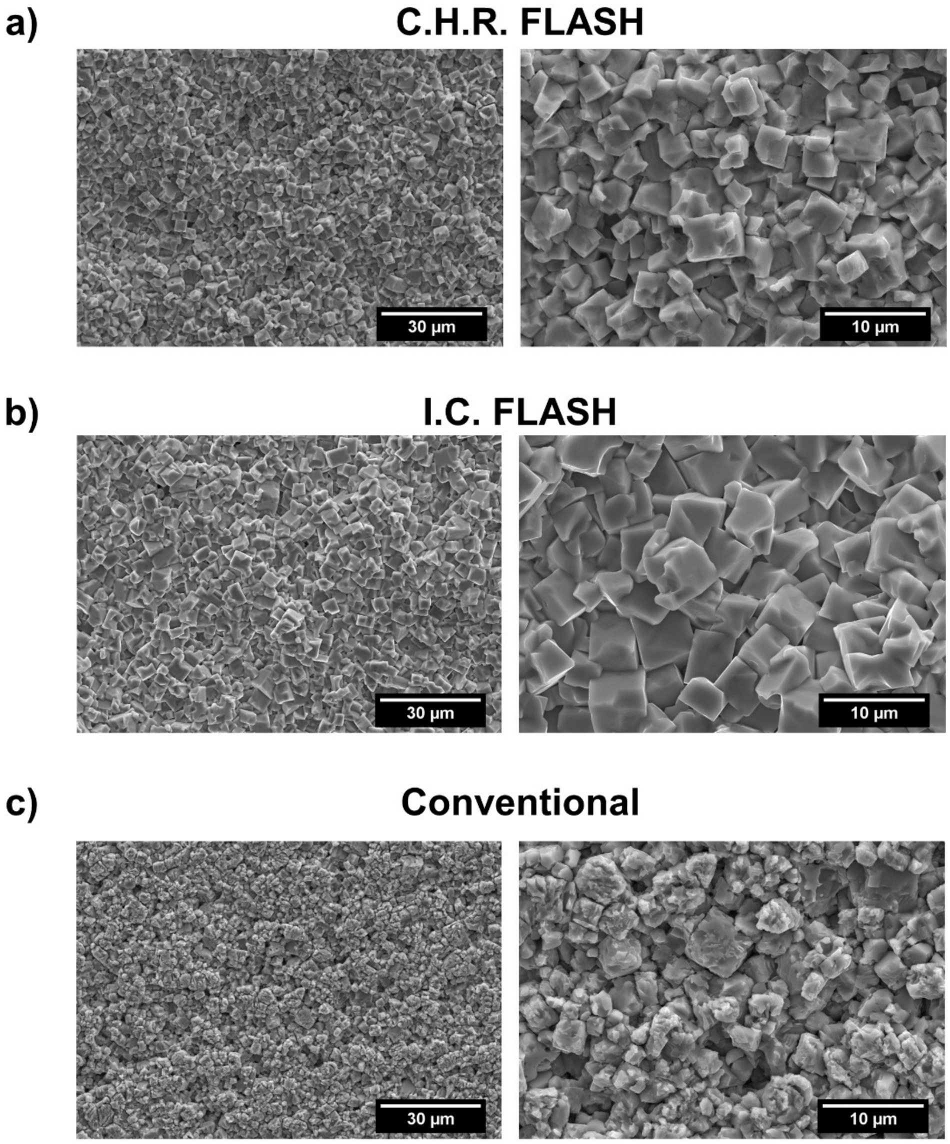
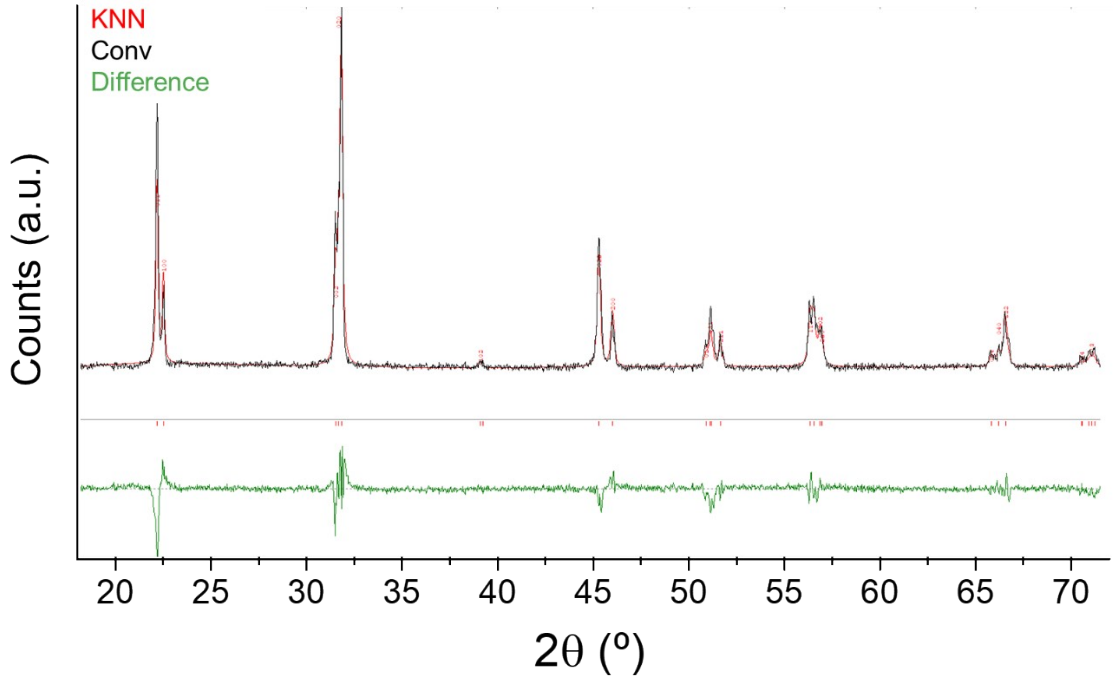


Figure S2 – Scanning electron microscopy (SEM) micrographs of a) C.H.R. FLASH, b) I.C. FLASH and c) conventionally sintered KNN ceramics, acquired with a 15 keV accelerating voltage at different magnifications, 1000 and 3000 times, left and right, respectively, *from [6] R. Serrazina, A. M. O. R. Senos, L. Pereira, J. S. Dean, I. M. Reaney, and P. M. Vilarinho, "The Role of Particle Contact in Densification of FLASH Sintered Potassium Sodium Niobate," Eur. J. Inorg. Chem., vol. 2020, no. 39, pp. 3720–3728, 2020.*

a)



b)

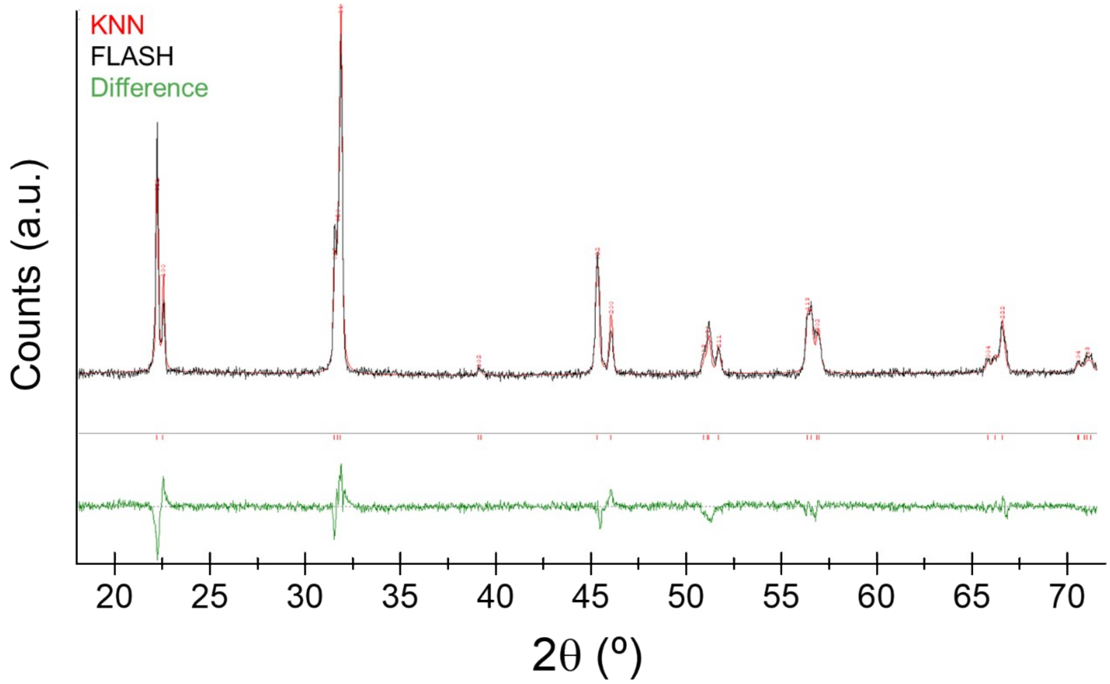


Figure S3 – Rietveld refinement results of XRD analysis of a) conventionally and b) FLASH sintered KNN. The black curve shows the experimentally obtained diffraction pattern, the red curve is the calculated pattern and the green curve reveals the difference.

COMSOL Multiphysics was used to develop the Finite Element Model for the simulation of both current density distribution and respective temperature (due to heating by Joule effect). [26]. The DC electrical conductivity of conventional KNN ceramics was accessed using a Keithley 2410 electrometer, with a 1 V/cm applied electric field. Platinum electrodes were painted and sintered on opposite faces of the ceramics prior to measurement. A constant heating rate of 10 ºC/min up to 1000 ºC was employed and the conductivity as a function of temperature is shown in Figure S4. The electrical conductivity of KNN was subsequently extrapolated for T > 1000 ºC based on an Arrhenius fit to the data. Measurements on several different conventionally sintered ceramics were performed, and the results were consistent and considered to be representative of KNN ceramics.

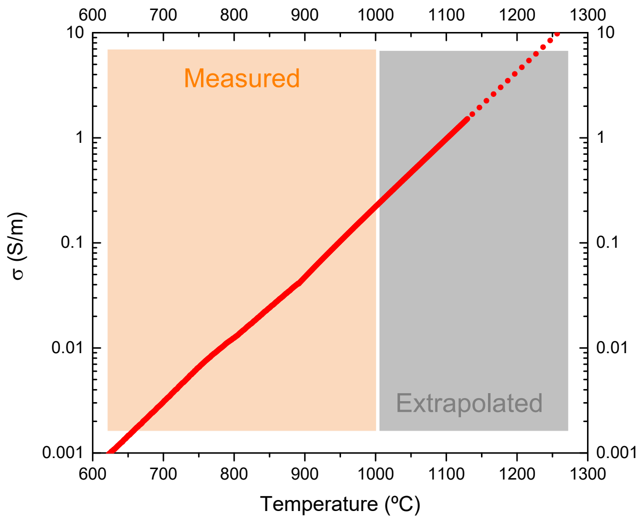


Figure S4 - Measured KNN conductivity σ (S/m) over measured temperature (with a 10 ºC/min heating rate) under an applied electric field of 1 V/cm.

To simulate the FLASH process, the sample holder and respective green KNN compact were described, as shown in Figure S5. For simulation, the green compact was approximated to a single 15 x 5 mm^2 monolithic block of material, identified as *KNN* in Figure S4. Thickness was not considered as only a 2D model was developed. The bi-dimensional approximation allows faster simulation times without compromising the results. KNN (with the respective electrical conductivity) was modelled to establish a perfect contact with two opposite platinum electrodes, that were also in contact with alumina parts, as in the experimental setup [28].

The FLASH process simulation was achieved using a *Terminal* function to one electrode, and a *Ground* function to the opposite electrode. A 300 V/cm electric field was scaled to the *terminal-ground* functions and the current was calculated and simulated as with respect to temperature and conductivity. To allow heat dissipation, the modelled setup was considered to be in air. Alumina electrical conductivity was taken as constant (10^{-12} S/m), while the thermal conductivity of KNN and alumina was considered temperature dependent and equal to 2.6 W/(m.K) and 27 W/(m.K), respectively. The time dependent model was run at a starting temperature of 900 ºC, representative of furnace equilibrium temperature before the application of the electric field. The results of current density and temperature profile were recorded at 1 s time intervals and are shown in Figure 5.

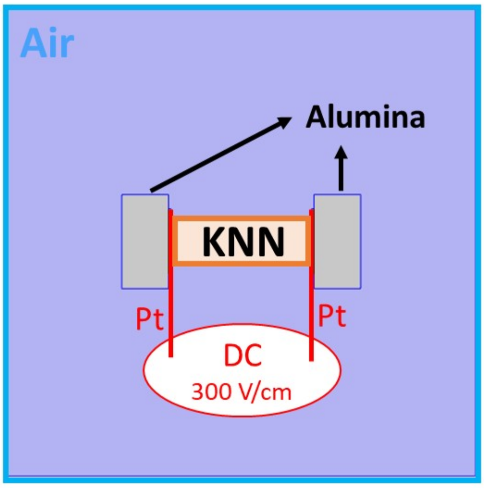


Figure S5 - Schematic representation of the model.