

# Dielectric properties of low temperature sintering by SPS of piezoelectric lead free (K,Na)NbO<sub>3</sub> ceramics

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Piezoelectric materials are a rapidly growing field of research and development, with potential applications in energy harvesting. Due to their outstanding electromechanical capabilities, Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> (PMN) and Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub> (PZT) have been the two main piezoelectric materials studied over the last decades. However, these two materials are lead-based compounds that should be replaced, due to environmental concerns about Pb and PbO toxicity, and today's leading lead-free candidates are (K,Na)NbO<sub>3</sub>(KNN), (Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub> (BNT), and (Ba,Ca)(Zr,Ti)O<sub>3</sub> (BCZT). In particular, KNN is the one with most promising chances to replace PZT.

Dense KNN ceramics require relatively high sintering temperatures, which are incompatible with the volatility of alkaline elements. Alternate processing techniques are thus required, such as Spark Plasma Sintering (SPS). SPS enables a significant reduction in both sintering temperatures and duration compared to conventional sintering. Here, we present the dielectric properties and polarization of KNN ceramics sintered at low temperature by SPS.

First, SPS was used to sinter disk-shaped ceramics from nanometer grain size commercial KNN powder (grain size < 100 nm). We were able to sinter KNN achieving relative densities higher than 95% with sintering temperatures lower than 700  C. As a result, the post-annealing, usually performed after SPS, was avoided; thus, reducing the global energy budget even further. The impact of the SPS experimental conditions (temperature, pressure, thermal ramps, environment...) on both the density and the dielectric properties are discussed. For sake of comparison with results from literature, a ceramic sintered by SPS at 1000  C, 100  /min, 40 MPa for 5 minutes and annealed at 1000  C for 8h was investigated. The piezoelectric coefficient  $d_{31}$  was evaluated using the following relationship  $d_{31} = k_{31}\sqrt{\epsilon_{11} * s_{11}}$ , and considering  $\epsilon_{11} = 600$  (measured far from the resonance) obtaining  $d_{31} = -62$  pC/N, which is comparable with the literature. Moreover, piezoelectric coefficient  $d_{33}$  was measured obtaining 63 pC/N. Furthermore, high temperature dielectric measurements and ferroelectric hysteresis loops performed on all low temperature sintered KNN ceramics are presented.