



# Microstructural, structural, dielectric and piezoelectric properties of potassium sodium niobate thick films

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The paper is dedicated to the memory of Professor Dr. Marija Kosec, whose ability to see further was an inspiration for this study.

## Abstract

In the framework of a systematic study, we present the influence of processing parameters – in particular the presence of a packing powder during sintering and the sintering temperature – on the microstructural and structural properties of potassium sodium niobate ( $K_{0.5}Na_{0.5}NbO_3$  or KNN) thick films. These KNN thick films were prepared with a 1 mass% addition of potassium sodium germanate (KNG), which serves as a liquid-phase sintering aid. The sintered films exhibited preferential crystallographic orientations along  $[100]_{pc}$  and  $[10-1]_{pc}$ , the origin of which lies in the compressive stresses developed during cooling as a result of the thermal expansion mismatch between the film and the substrate. In addition, the dielectric permittivity, dielectric losses and the piezoelectric  $d_{33}$  coefficient of the obtained films were compared with those of KNN bulk ceramics. © 2013 Elsevier Ltd. All rights reserved.

**Keywords:**  $K_{0.5}Na_{0.5}NbO_3$ ; Thick film; Sintering; Orientation; Lead-free piezoelectric

## 1. Introduction

$K_{0.5}Na_{0.5}NbO_3$  (KNN) is an important, lead-free, ferroelectric material that is biocompatible and exhibits a large piezoelectric response, especially when chemically modified with Li, Sb and Ta.<sup>1,2</sup> Presently, KNN represents one of the most promising environmentally friendly substitutes for lead-based ceramics, such as lead zirconate titanate ( $Pb(Zr,Ti)O_3$  or PZT) and lead magnesium niobate–lead titanate ( $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$  or PMN–PT).<sup>3,4</sup>

The electromechanical response of KNN is reported to be inferior to that of PZT or PMN–PT, but KNN still possesses some interesting properties. The unmodified KNN ceramics have a piezoelectric  $d_{33}$  coefficient typically between 80 and 110 pC/N.<sup>5,6</sup> Additionally, it was reported by Tran-Huu-Hue et al. that Sr-doped KNN exhibits a high, longitudinal, sound velocity (5800 m/s), a low acoustic impedance (24 MRayl) and

a low dielectric constant (280), all of which makes KNN suitable for high-frequency applications.<sup>7</sup> Despite the potential of KNN for transducer applications, which would require KNN in a thick-film form, the processing and functional properties of KNN thick films have been studied to a much lesser extent<sup>8–16</sup> than KNN thin films and bulk ceramics.

In contrast to bulk ceramics, the thick films are characterized by constrained sintering – their densification is hindered due to the clamping of the film to a rigid substrate.<sup>17,18</sup> In general, constrained sintering poses a serious problem in terms of achieving high film densities. At present, none of the reports on KNN thick films has treated this problem systematically.<sup>8–16</sup> The most common and, probably, the simplest way to improve the densification of KNN is the addition of a liquid-phase sintering aid.<sup>19–25</sup> Potassium sodium germanate (KNG), which was developed by our group, was proved to promote the sintering of both KNN ceramics and thick films.<sup>19,26</sup>

In addition to constrained sintering, the thick films are characterized by a large surface-to-volume ratio; in contrast to bulk ceramics, the films are, therefore, more likely to lose volatile species due to sublimation during annealing at high temperatures. In the case of lead lanthanum zirconate titanate (PLZT)

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thick films it was observed that higher film densities were achieved for the films sintered with the packing powder (PP).<sup>27</sup> In fact, the combination of 1% liquid-phase sintering aid, i.e., an excess of PbO in PLZT, and the PP yielded films with higher densities than when adding 6% liquid-phase sintering aid only, without the PP. In the same paper the authors explained the role of the PP in terms of an atmosphere adjustment during sintering, i.e., the PP provided volatile species in the vapour phase in sufficient quantity to significantly reduce their sublimation from the films. Consequently, the films made in the presence of the PP were dense, phase-pure and defect-free. In contrast to the lead-based systems, no systematic studies were done, so far, on the role of the PP or the temperature on the sintering of the KNN thick films.

Recent studies by Uršič et al.<sup>28</sup> on PMN–PT thick films revealed that the compressive stresses developed during cooling of the thick-film structure, which are created as a result of the thermal-expansion mismatch between the substrate and the actual film, relaxed by shifting the morphotropic phase boundary (MPB), i.e., by changing the relative content of the tetragonal and monoclinic phases. In contrast to PMN–PT, KNN does not exhibit any major symmetry changes around the composition with the Na/K ratio equal to 1, which should be characteristic for a material with an MPB.<sup>29</sup> Consequently, it is expected that the thermal-stresses relaxation mechanism in KNN, not studied thoroughly so far, would be different from that observed in PMN–PT.

In this paper we demonstrate the importance of the packing powder (PP) when it comes to obtaining phase-pure KNN + KNG thick films. In addition, we also present a systematic study of the influence of the sintering temperature on the microstructural and structural properties of KNN + KNG thick films, focusing particularly on the effect of the thermal stresses in the films. With the aim being to get a better understanding of the electrical and electromechanical properties of the KNN thick films, the dielectric and piezoelectric properties of the KNN thick films and bulk ceramics are compared and discussed.

## 2. Experimental

### 2.1. Powders

The KNN powder was prepared by a conventional solid-state route from a mixture of  $K_2CO_3$  (99+%, Alfa Aesar, Ward Mill, MA, USA),  $Na_2CO_3$  (ACS reagent, 99.95–100.05%, Sigma–Aldrich, St. Louis, MO, USA) and  $Nb_2O_5$  (99.9%, Sigma–Aldrich, St. Louis, MO, USA). Prior to the synthesis, the carbonates were dried at 200 °C for 2 h and milled for 3 h in acetone using a 250-mL polyethylene (PE) vial, filled with 350 g of yttria-stabilized-zirconia (YSZ) milling balls with a diameter of 3 mm. The masses of the milled  $K_2CO_3$  and  $Na_2CO_3$  were 40 and 50 g, respectively. We used a planetary mill (Retsch, model PM400, Haan, Germany), which was set at 175  $min^{-1}$  of the main-disc rotational frequency. The  $Nb_2O_5$  was used as received.

The starting powders were weighed in a dry atmosphere using a glove bag (Alfa Aesar, Ward Mill, MA, USA) in a molar ratio of

$K/Na/Nb = 1/1/2$ . A batch of 35 g of the mixture of the reagents was then homogenized for 4 h in acetone using a 125-mL YSZ vial, filled with 150 g of YSZ milling balls with a diameter of 3 mm. We used a planetary mill set at 175  $min^{-1}$  of the main-disc rotational frequency.

The solid-state synthesis was performed in two calcination steps, i.e., the first calcination was performed at 800 °C for 4 h, while the second one was at 750 °C for 4 h. In both cases the powder was calcined in a closed alumina crucible and the heating/cooling rates were 5 K/min. The planetary milling was applied after both calcinations using the same conditions as for the homogenization of the reagent mixture.

The KNG liquid-phase sintering aid was prepared according to Bernard et al.<sup>19</sup> A total of 1 mass% of KNG was added to the KNN and 14 g of this mixture were homogenized for 4 h in acetone using a 50-mL PE vial, filled with 90 g of YSZ milling balls with a diameter of 3 mm. The planetary mill was set at 175  $min^{-1}$  of the main-disc rotational frequency. The mixture of KNN and 1 mass% KNG is subsequently denoted as KNN + 1KNG.

### 2.2. Bulk ceramics

Powder compacts of KNN and KNN + 1KNG were prepared by uniaxial pressing at 50 MPa, followed by isostatic pressing at 200 MPa. The KNN + 1KNG ceramics were prepared by sintering the powder compacts on a Pt foil in a closed alumina crucible for 2 h at 1100 °C with heating/cooling rates of 5 K/min.

### 2.3. Thick films

Platinized alumina substrates were prepared by screen-printing the commercially available platinum pastes (ESL, 5542, King of Prussia, PA, USA; DuPont, 9896 Wilmington, DE, USA) onto optically polished alumina plates with dimensions 30 mm × 30 mm × 3 mm. Subsequently, the substrates were sintered for 1 h at 1200 °C with heating/cooling rates of 5 K/min.

The ink was prepared by mixing the KNN + 1KNG powder and a terpeneol-based organic vehicle and screen-printed onto the platinized alumina substrates. The KNN + 1KNG thick films were prepared by screen-printing four layers, each one on top of the other, in sequence. After each deposition step the films were dried at 150 °C for 15 min. The as-deposited and dried KNN + 1KNG thick films were cold isostatically pressed at 300 MPa. The thickness of the KNN + 1KNG thick films, as determined using confocal microscopy, was ~60  $\mu m$ . The films were sintered for 2 h at temperatures of 1000 °C, 1050 °C and 1100 °C. Selected films were sintered in the presence of the PP, i.e., powder with the same chemical composition as the films. The heating/cooling rates were 5 K/min.

### 2.4. Characterization

The densities of the ceramic compacts were determined using Archimedes' method. For the calculation of the relative density we used the values of the theoretical density of KNN and potassium and sodium germanate from the literature.<sup>5,30–33</sup>

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