



# Microstructure of sodium-potassium niobate ceramics sintered under high alkaline vapor pressure atmosphere

Jérôme Acker<sup>a,1</sup>, Hans Kungl<sup>a,b,\*</sup>, Roland Schierholz<sup>b</sup>, Susanne Wagner<sup>a</sup>,  
Rüdiger-A. Eichel<sup>b</sup>, Michael J. Hoffmann<sup>a</sup>

<sup>a</sup> Institute for Applied Materials – Ceramics in Mechanical Engineering, Karlsruhe Institute of Technology, Haid- und-Neu-Straße 7, 76131 Karlsruhe, Germany

<sup>b</sup> Forschungszentrum Juelich, Institute of Energy and Climate Research IEK-9, Ostring 10, 52425 Juelich, Germany

Received 14 April 2014; received in revised form 13 June 2014; accepted 19 June 2014

Available online 16 July 2014

## Abstract

One of the most challenging steps in processing sodium potassium niobate (KNN) ceramics is sintering. At temperatures close to the solidus line, the high volatility of the alkaline becomes an issue of major concern for the sintering process. While alkaline evaporation is frequently related to difficulties in densification, few work on the effects of alkaline vapor pressure on microstructure have been reported. KNN materials with alkaline/niobium ratios ranging from 1.02 to 0.98 were sintered at 1105 °C. Two different sintering setups were used. An alkaline rich sintering atmosphere was provided when sintering the materials embedded in  $(K_{0.5}Na_{0.5})_{1.02}NbO_3$  powder, while reference ceramics were sintered in loosely covered crucibles. Resulting from the alkaline content in the sintering atmosphere a shift toward microstructures considered typical for batch compositions with higher alkaline content was detected. Densities decrease for KNN with alkaline excess and stoichiometric KNN, whereas they tend to increase for niobium excess material.

© 2014 Elsevier Ltd. All rights reserved.

**Keywords:** Ferroelectrics; Lead-free ceramics; Microstructure; Sintering; Piezoelectrics

## 1. Introduction

Among the obstacles hindering industrial production of lead free ferroelectric devices based on KNN ceramics a major aspect is the difficult densification of these perovskite ( $ABO_3$ ) materials.<sup>1–5</sup> Almost complete densification close to the theoretical density of  $\rho_{th} = 4.51 \text{ g/cm}^3$  was achieved so far by hot pressing,<sup>6</sup> spark plasma sintering (SPS)<sup>7–10</sup> or by sintering at temperatures up to 1200 °C in the solid–liquid coexistence region.<sup>11</sup> Sintering of stoichiometric KNN under atmospheric pressure when remaining in the solid state regime results in densities from 3.9 to 4.3  $\text{g/cm}^3$ .<sup>12–15</sup> Generally there is a pronounced influence on densification behavior and microstructure from

the alkaline/niobium (A/B) ratio of the batch composition.<sup>16–18</sup> Recent progress in controlling the stoichiometry in preparation of the batch composition was provided by the approach to use alkaline hydrogen carbonates instead of  $K_2CO_3$  and  $Na_2CO_3$  raw materials.<sup>19</sup> The activation of sintering by slight B-site excess in order to obtain enhanced diffusion via the creation of A-site vacancies can be a viable approach for better densification under suitable conditions.<sup>20</sup> The sintering atmosphere also plays an important role for densification. Several mechanisms of influence of the sintering gas atmosphere on microstructure and densification have to be considered. First the sintering atmosphere determines the equilibrium vacancy concentration for a given batch composition via the influence of the oxygen partial pressure. Second, the type of sintering gas affects the evaporation of alkalines, which in turn modifies the alkaline/niobium stoichiometry of the ceramics and the conditions for film formation at the grain boundaries. The effects of sintering gas atmosphere on microstructure have been discussed by Fisher and Kang.<sup>21</sup> KNN materials prepared from  $C_4H_4KNaO_6 \cdot 4H_2O$  and  $Nb_2O_5$  were sintered in  $O_2$ ,  $N_2$ , 75% $N_2$ –25% $H_2$  and  $H_2$ . By adding

\* Corresponding author at: Forschungszentrum Juelich, Institute of Energy and Climate Research IEK-9, Ostring 10, 52425 Juelich, Germany. Tel.: +49 2461 61 6185; fax: +49 2461 61 9747.

E-mail address: [h.kungl@fz-juelich.de](mailto:h.kungl@fz-juelich.de) (H. Kungl).

<sup>1</sup> Present address: Continental Automotive GmbH, Siemenstraße 12, 93055 Regensburg, Germany.

calcined KNN atmosphere powder to the sintering batches it was attempted to control the evaporation. Fisher and Kang found a reduction and a time delay of abnormal grain growth when sintering in reducing  $H_2$  rich atmosphere which they attributed to an increase in vacancy concentration. Without controlling the alkaline vapor pressure, another mechanism emerging from the sintering gas atmosphere on densification and microstructure is its influence on alkaline evaporation.<sup>13,22</sup> Stannek measured reduced mass losses when sintering under oxygen compared to sintering in air<sup>23</sup> as well as enhanced evaporation of alkalis in presence of humidity. This was also reported by Flückiger and Arend.<sup>24</sup> Sintering in oxygen results in enhanced densities of KNN ceramics, according to experiments described by Stannek.<sup>23</sup> Malic et al.<sup>25</sup> and Kosec et al.<sup>13</sup> consider oxygen atmosphere and dry conditions to be a key issue for sintering KNN ceramics with favorable densities and microstructure. DFT calculations by Koerbel et al.<sup>26</sup> indicate, that the oxygen vapor pressure during processing Cu-doped KNN may influence the site occupancy and the charge state of the copper in the KNN lattice. While there are pronounced effects on alkaline evaporation already from changes in the sintering gas atmosphere, even more and direct influence on the alkaline vapor pressure can be put forth by adding alkaline rich atmosphere powder to the sintering batch. Zhen and Li<sup>27,28</sup> reported on the fabrication of dense KNN ceramics by application of a double crucible setup using atmosphere powders to prevent alkaline evaporation. In recent work on dielectric properties of KNN sintered with vs. KNN sintered without atmosphere powders Liu et al.<sup>29</sup> suggested that sintering under high alkaline vapor pressure decreases the concentration of oxygen vacancies, leads to singly ionized oxygen vacancies and increases the activation energies for oxygen hopping, so the electrical conductivity generated by oxygen vacancies is reduced. Recent work of Pavlic et al.<sup>30</sup> compares the microstructures of KNN + 1 mass% potassium sodium germanate thick films sintered at 1100 °C without and in presence of packing powder with composition identical to those of the thick films. While sintering without packing powder results in ceramics with irregularly shaped grains and a wide distribution of grain size, the ceramics sintered using packing powder are cuboidal and show a uniform grain size distribution. However, the density was lower and the pore size was larger in the thick films sintered with packing powder.<sup>30</sup> Owing to costs related to production and waste disposal there is little affinity to use types of sintering procedures which involve the use of atmosphere powders for industrial production. On the other hand, fluctuations in alkaline vapor pressure within conventional sintering procedures emerge from technical characteristics such as batch size, position of the material in the furnace and gas flow conditions. Therefore insight in the effects of the alkaline vapor pressure on sintering, microstructure and electrical properties of these materials is required. The primary objective of the present paper is to investigate the influence of high alkaline vapor pressure on microstructure of KNN. KNN samples with different alkaline/niobium ratios of the batch compositions were sintered (i) in a conventional sintering setup in air and (ii) when buried in  $(K_{0.5}Na_{0.5})_{1.02}NbO_3$  atmosphere powder. The microstructures of both types of

materials were analyzed by SEM for each batch composition. From observations of the microstructure and density measurements conclusions with respect to the sintering are drawn and discussed.

## 2. Experimental

KNN with 2 mol% A-site excess, stoichiometric KNN and KNN with 0.5 mol% and 2 mol% B-site excess corresponding to batch compositions of  $(K_{0.5}Na_{0.5})_{1.02}NbO_3$ ,  $(K_{0.5}Na_{0.5})NbO_3$ ,  $(K_{0.5}Na_{0.5})_{0.995}NbO_3$ ,  $(K_{0.5}Na_{0.5})_{0.98}NbO_3$  were prepared by a solid state route using high purity raw powders.<sup>16</sup> Dry forming of cylindrical green bodies (1.8 g powder, 12 mm diameter dye matrix) by uniaxial pressing and subsequent cold isostatic pressing at 400 MPa resulted in green densities between 2.80 and 2.95 g/cm<sup>3</sup> for stoichiometric and B-site excess KNN, while densities between 3.20 and 3.35 g/cm<sup>3</sup> were obtained for the A-site excess KNN.

Ceramics were sintered at 1105 °C/2 h in a furnace (Gero Hochtemperaturöfen GmbH, Neuhausen, Germany) using two different sintering setups, both under air. Applying conventional sintering conditions ceramics were placed in alumina crucibles (28.2 cm<sup>3</sup> volume) and loosely covered with an alumina plate. For sintering under high alkaline vapor pressure smaller (9.4 cm<sup>3</sup> volume) cylindrical alumina crucibles with precision ground covers, thus corresponding almost to sealed crucibles, were used. The samples were buried in  $(K_{0.5}Na_{0.5})_{1.02}NbO_3$  atmosphere powder, filling first 0.5 g of the atmosphere powder on the bottom, then placing the green bodies, and finally filling the gaps between the sidewall of the crucible and the samples and covering their top by 1.5 g of atmosphere powder. The total amount of atmosphere powder thus amounted to 2 g corresponding to a weight ratio of 1.1 between atmosphere powder and samples. Heating and cooling rates were 3 °C/min in both types of sintering experiments. Weight losses during sintering were determined only for the samples sintered with the conventional setup, because owing to the direct contact to the sintering bodies particles of the atmosphere powder remained attached to the sample after sintering. Thus no reliable information on weight changes in the samples sintered under powder bed could be obtained. Densities of all samples were measured by the Archimedes method in isopropanol. The microstructure of the ceramics was analyzed by scanning electron microscopy using a Leica Stereoscan 440 instrument. SEM samples were prepared by cutting circular disks from the cylindrical samples, embedding them in epoxy resin and following standard polishing procedures. All mechanical treatment was carried out using water-free, oil based polycrystalline diamond suspensions (ATM). SEM images were recorded from the polished surfaces after chemical etching with a solution of  $H_2O-HCl-HF$  and sputtering thin Au-layers to prevent charging under the electron beam. Atomic composition of the matrix and secondary phase in the 2 mol% B-site excess KNN ceramics were investigated qualitatively analyzing the EDX spectra. A Röntec EDR 288 spectrometer equipped with a UHV Deware Si(Li) Detector was used for these measurements.

Download English Version:

<https://daneshyari.com/en/article/1474276>

Download Persian Version:

<https://daneshyari.com/article/1474276>

[Daneshyari.com](https://daneshyari.com)