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# Investigation of phase boundaries in the system $(K_xNa_{1-x})_{1-y}Li_y(Nb_{1-z}Ta_z)O_3$ using high-throughput experimentation (HTE)

Tobias A. Stegk, Henry Mgbemere, Ralf-Peter Herber, Rolf Janssen, Gerold A. Schneider *

*Institute of Advanced Ceramics, Hamburg University of Technology, Denickestr. 15, 21073 Hamburg, Germany*

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**Abstract**

A high-throughput experimental (HTE) approach starting from dry, fine-grained powders was used to synthesize bulk samples in the system $(K_xNa_{1-x})_{1-y}Li_y(Nb_{1-z}Ta_z)O_3$, a doped variant of the piezoelectric $(K_{0.5}Na_{0.5})NbO_3$ (KNN). Starting from the system $(K_{0.5}Na_{0.5})_{1-y}Li_y(Nb_{1-z}Ta_z)O_3$ known from the works of Saito et al. an effort was made to establish a higher order phase diagram. Special emphasis was put on expanding the known morphotropic phase boundary that constitutes a region of special interest for electroceramic materials as it features maximum piezoelectric properties. Analyses were performed using a HTE-compatible technique, namely automated powder X-ray diffraction (XRD).


*Keywords:* KNN; Powders-solid state reaction; Mixing; Niobates; Actuators; High-throughput experiemtation

## 1. Introduction

High-throughput experimentation (HTE) has been explained as "a set of techniques for creating a multiplicity of compounds and then testing them for activity".[1] It has been applied extensively for the development and optimization of ceramics mostly on the basis of thin-film technology since that allows for an easy continuous change of compositions and is therefore best suited for HTE.[1,2] For ceramic applications where macroscopic bulk properties are most important, e.g. in multilayer stack actuators, a different processing route is necessary. To emulate the most common powder metallurgical synthesis for ceramic materials, namely the conditioning, shaping and heat-treatment of powders, an HTE-setup has been conceived that has the capacity to produce libraries of up to 40 bulk samples at a time.[3] Drawing on the example of the yttria toughened zirconia polycrystal (Y-TZP) system, it was shown in Ref. 3 that it was possible to produce Y-TZP samples with a resolution of 0.5 mol.% and an experimental error of ∼1 mol.% pertaining to yttria content. Synthesis and analysis were performed in high-throughput mode using dry ceramic powders as starting material.

In the present study, the dry powder HTE-setup was used to synthesize a variant of the system sodium potassium niobate ($K_{0.5}Na_{0.5}NbO_3$, KNN), a piezoelectric material that has the potential to substitute for lead zirconate titanate ($Pb(Ti_{1-x}Zr_x)O_3$, PZT) and hence to be used in the future in electronic appliances in the form of transducers or sensors.

PZT, a solid solution of $PbZrO_3$ and $PbTiO_3$, has been widely used in the manufacture of actuators, sensors, transducers and in other electromechanical devices because of its excellent piezoelectric properties. For commercial PZT-materials $x \approx 0.48$ which is coincident with a morphotropic phase boundary (MPB) between a rhombohedral and a tetragonal phase resulting in a maximum for the piezoelectric behaviour.[4] For actuator purposes the small signal $d_{33}$ (piezoelectric coefficient) is used most often as a measure to compare the potential of different piezoceramics. As a benchmark for alternatives to PZT a $d_{33}$ value of 300 pC/N is necessary. Additionally, the Curie temperature should be above 150 °C.

A substantial constituent of PZT however is formed by lead which is precarious since elemental lead is highly toxic. Due to its volatility it is released to the atmosphere during heat-

* Corresponding author. Tel.: +49 40 42878 3037; fax: +49 40 42878 2647.
*E-mail address:* g.schneider@tu-harburg.de (G.A. Schneider).

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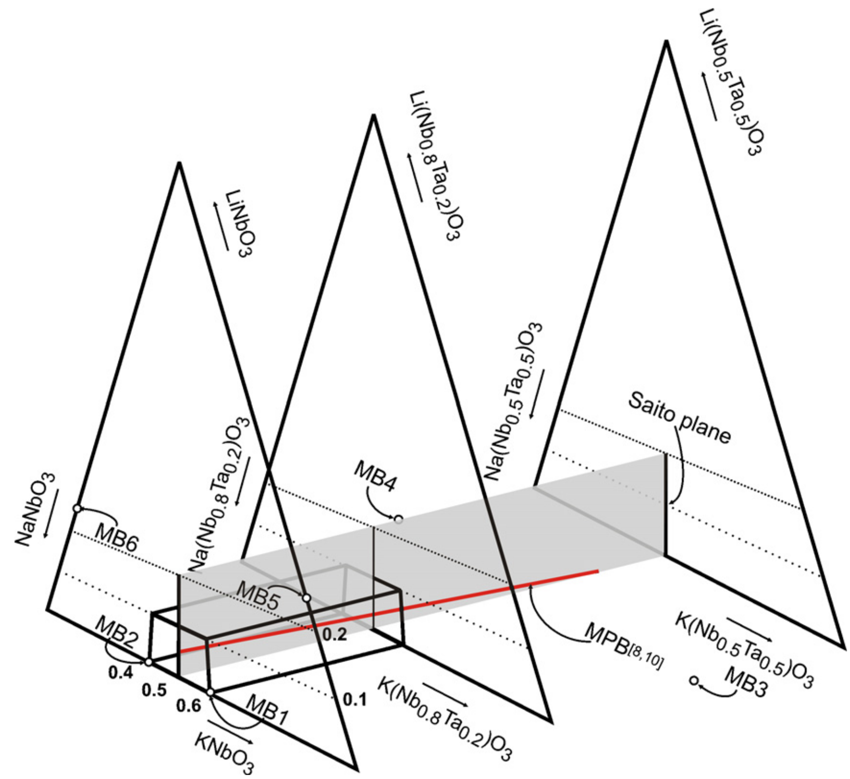


Fig. 1. Scheme of ternary phase diagram of $(K_xNa_{1-x})_{1-y}Li_y(Nb_{1-z}Ta_z)O_3$. The shaded area is the concentration plane examined in Refs. 8,10 here termed Saito-plane. The line located on the Saito-plane shows the approximate progression of the known morphotropic phase boundary. The dots labeled MB1-6 are the masterbatches used in the high-throughput synthesis of the library. The volume depicted between $RNbO_3$ and $R(Nb_{0.8}Ta_{0.2})O_3$ with R = K, Na, Li is the experimental space investigated in the present work.

treatment and furthermore it causes problems with respect to the disposal of PZT-based products at the end of their life cycle. The European Union has reacted on these environmental concerns by legal restrictions on the use of toxic lead.[5] These legal alterations have spawned interest in finding a lead-free replacement for PZT ceramics. Under amplified investigation is the perovskite family of KNN[6] for which three MPBs are reported in the literature so far, two in the system $K_xNa_{1-x}NbO_3$[7] and one in the system $(K_{0.5}Na_{0.5})_{1-y}Li_y(Nb_{1-z}Ta_z)O_3$.[8] Recently, the morphotropic nature of the phase boundary in the latter system separating an orthorhombic and tetragonal phase field could be verified experimentally[9] and $d_{33}$ values between 200 and 300 pC/N have been reported along the MPB.[8,10] However, only for KNN prepared by a special texturisation procedure could maximum piezoelectric properties be achieved ($d_{33}$ > 300 pC/N).[8] It is evident, that the textured synthesis of materials is complex and an implementation in cheap mass production is hence questionable. Furthermore, it is well known that KNN shows massive impediments in synthesis, namely difficulties when sintering and also the material's instability in air stemming from high reactivity with moisture has been reported.[11,12] Hence, the aspiration for replacement of PZT by a KNN-system necessitates efforts to overcome said impediments and to further optimize piezoelectric behaviour of conventionally synthesized KNN-materials.

Most of the investigations so far have been inside of or in close vicinity to the "Saito-plane", i.e. the concentration plane $(Na_{0.5}K_{0.5})_{1-y}Li_y(Nb_{1-z}Ta_z)O_3$ with $y \in [0,0.2]$ and $z \in [0,0.6]$ where the MPB was identified to behave approximately according to

$$y = 0.05 - 0.11z \quad (1)$$

It is obvious that the extension of this MPB line into a two-dimensional MPB area by opening the space in $x$-direction, i.e. changing the K/Na-ratio, offers new opportunities to find better piezoelectric compositions.

Consequently, this paper reports on the systematic expansion of the Saito-plane already investigated in Refs. 8,10 towards a concentration volume as depicted in Fig. 1. This concentration volume necessitates at least 100 different compositions for the respective phase space to be scanned sufficiently. As a consequence it is ideally suited for an HTE approach. Originating from the known location of the MPB line in the Saito-plane, the progression of the MPB into the mentioned concentration volume was determined on the basis of X-ray diffraction data.

## 2. Experimental

Initially six masterbatches for the HTE-procedure were synthesized using a conventional mixed carbonate and oxide route. $Li_2CO_3$, $Na_2CO_3$ and $K_2CO_3$ (99+% purity, ChemPur GmbH, Karlsruhe, Germany) as well as $Nb_2O_5$ and $Ta_2O_5$ (99.9% purity, ChemPur GmbH, Karlsruhe, Germany) were used as raw powders. All powders were dried at 200 °C