

## Alkaline-Earth Doping in (K,Na)NbO<sub>3</sub> Based Piezoceramics

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### **Abstract:**

In this contribution the effect of alkaline-earth (AE) dopants Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> on sinterability and functional response of KNN is studied. Ceramic powders with the general formula (K<sub>0.5</sub>Na<sub>0.5</sub>)<sub>1-2y</sub>AE<sub>y</sub>NbO<sub>3</sub>,  $y = 0.005$  were prepared by classical ceramic processing. The values of 94 - 95 % of theoretical density (TD) are obtained for stoichiometric KNN after sintering at 1115 °C for 2 hours. Calcium and strontium doping promotes densification while magnesium doping inhibits it. In the case of Ba-doping a secondary phase forms.

The dielectric constant and piezo  $d_{33}$  coefficient determined by Berlincourt piezo  $d_{33}$ -meter of Ca and Sr-doped KNN ceramics are 500 and 95 pC/N, respectively, while the values for undoped KNN are slightly lower.

**Keywords:** B. X-ray methods, C. Piezoelectric properties, D. Niobates,

### **Introduction**

Piezoelectric materials based on Pb(Zr,Ti)O<sub>3</sub> solid solution (PZT) have been widely used due to their piezoelectric, pyroelectric and ferroelectric properties. One of the major drawbacks of these materials, however, is their high lead content: the ceramics contain about 60 weight % lead, and therefore represent a possible ecological hazard. As a consequence much of the current research is oriented towards more environmentally friendly lead-free materials. An alternative group of lead-free ferroelectric materials are those based on the sodium potassium niobate (K,Na)NbO<sub>3</sub> solid solution, with the composition K/Na 50/50 being close to the

morphotropic phase boundary and exhibiting a moderate dielectric constant and an optimum piezoelectric response.<sup>1-3</sup>

One of the major problems of KNN is sintering: according to early reports the stoichiometric material is extremely difficult to consolidate<sup>1</sup>. Various strategies have been used to overcome this problem. Hot pressing or hot isostatic pressing has been used to achieve high densities as early as in 1960's<sup>4,5</sup>. Kosec and Kolar prepared KNN ceramics sintered at 1125 °C for 24 h with 97.1 % theoretical density (TD = 4.51 gcm<sup>-3</sup>), by introducing Mg-ion (1%) as A-site dopant as compared to 94.5 % for the stoichiometric composition. Similarly, an improvement in density was achieved by introducing Nb-excess. By both ways they introduced A-site vacancies into the perovskite lattice and therefore promoted sintering<sup>6</sup>. Promoted sintering of KNN with Nb-excess and therefore with an increased amount of A-site vacancies has also been confirmed in our recent work<sup>7</sup>. Ahn et al. used Ba-doping to promote densification; additions of up to 4 mole % Ba indeed increased the density, however, a Ba-rich secondary phase was observed after adding more than 1.5 mole % Ba<sup>8</sup>.

In this contribution the effect of a low amount of alkaline-earth(AE) dopants, 0.5 at.% Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> on KNN solid solution synthesis, sinterability and functional response of corresponding ceramics is studied. The AE ions Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> were chosen on the basis of the similarity of their ionic radii<sup>9</sup> to those of K<sup>+</sup> and Na<sup>+</sup>, while Mg<sup>2+</sup> ion is noticeably smaller than the alkaline ions (Table 1). We assumed that AE ions would substitutionally occupy the A-sites of the perovskite lattice in agreement with the general formula (K<sub>0.5</sub>Na<sub>0.5</sub>)<sub>1-2y</sub>AE<sub>y</sub>NbO<sub>3</sub>.

## Experimental

Pure and AE-doped KNN ceramics with the general formula (K<sub>0.5</sub>Na<sub>0.5</sub>)<sub>1-2y</sub>AE<sub>y</sub>NbO<sub>3</sub>, AE = Mg, Ca, Sr, Ba, y = 0.005 were prepared from sodium potassium tartrate tetrahydrate

$\text{KO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{Na} \times 4\text{H}_2\text{O}$  (99.5%, Fluka) and niobium oxide  $\text{Nb}_2\text{O}_5$  (99.9%, Aldrich). The dopants were introduced as nitrates:  $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$  (99%, Fluka),  $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$  (p.a., RdH),  $\text{Sr}(\text{NO}_3)_2$  (99,97%, Alfa),  $\text{Ba}(\text{NO}_3)_2$  (99+%, Aldrich). The 140 g batches were homogenized in acetone, calcined two times at 650 °C for 4 hours and milled to yield submicron sized powders, the median particle size typically at about 0.8  $\mu\text{m}$  as confirmed by laser granulometry. Powder compacts were uniaxially pressed with 300 MPa and sintered at 1115 °C for 2 hours in air.

Density was calculated from mass and dimensions of ceramic pellets. The phase composition was determined by X-ray diffraction (XRD) with Cu  $\text{K}\alpha$  radiation (Philips PW 1710, step: 0.02°) and using Si as the internal standard. The cell parameters were refined by the least-square method. A JEOL 5800 scanning electron microscope (SEM) with EDXS was used for the microstructural analysis of the polished samples.

Differential scanning calorimetry (DSC Netzsch 200) was used to follow the phase transformations of as-sintered ceramic pellets at a heating rate of 10 °C/min.

For electrical characterisation gold electrodes were applied. Capacitance and  $\tan \delta$  were measured at 10 kHz (Hewlett Packard 4192 LF Impadance Analyzer). The samples were poled with 2 kV/mm at 100 °C. The piezo  $d_{33}$  constant was determined by a Berlincourt piezo  $d_{33}$  meter (Take Control).

## **Results and Discussion**

After the solid state synthesis at 650 °C the KNN powder is orthorombic according to XRD, in agreement with the phase diagram <sup>1</sup>. Broadening of the peaks is attributed to a submicron particle size and also possibly to a not complete homogenization of the solid solution at 650°C. Doping with 0.5 at. % Mg, Ca and Sr yields single-phase powders, while doping with 0.5 % Ba causes the appearance of a secondary phase (Figure 1). Its peaks correspond to a

secondary phase observed by Powell in the study of calcination of the nitrate-derived Ba-doped KNN powder and nominated as  $(\text{NaK})\text{Nb}_8\text{O}_{21}$ <sup>10</sup>.

XRD spectra of the sintered materials are shown in Figure 2. The undoped and Mg, Ca and Sr doped KNN ceramics are single-phase perovskite, with orthorhombic syngony. Note however that trace amounts of secondary phase(s) could be present in all samples. The cell parameters based on the orthorhombic cell proposed by Stanek<sup>11</sup> of the undoped, Ca and Sr doped KNN differ on the level of uncertainty. The Mg-doped KNN is characterized by a slightly smaller volume of the unit cell (Table 2). The 0.5%Ba doped KNN contains beside the matrix perovskite phase, a noticeable amount of secondary phase or phases which could be ascribed to various alkaline or alkaline-earth alkaline polyniobates<sup>12,13</sup>.

The densities of the samples sintered at 1115 °C for 2 hours in air are collected in Table 2. The density of stoichiometric KNN is 94.4 % of TD. Doping with Mg causes a decrease in density to 90 % TD, Ca doping results in almost unchanged density, while doping with Sr leads to a 2 % higher density, about 96 %TD. The Ba-doped KNN, that contains a secondary phase, has got 94 % TD.

The polished microstructures of undoped and doped KNN ceramics are shown in Figure 3. We encountered a problem of pullouts during polishing which we ascribed to the rather large grain size (spanning to a few 10 μm) of the undoped, Ca and Sr doped samples and to the cubic morphology of the grains. On the level of SEM the undoped, Mg and Ca doped samples are single phase while in the case of Sr-doped KNN we detected some second phase inclusions. In the case of Ba-doping the polished microstructure reveals interlocking networks of two phases. According to EDXS the light-gray phase is niobium rich in comparison to the matrix phase, which is in agreement with the XRD results.

In order to further verify the incorporation of the AE-dopants into the perovskite cell we performed the DSC analysis assuming that the phase-transition temperatures are sensitive to

the stoichiometry. The DSC cooling curves of KNN samples are collected in Figure 4. According to the phase diagram, the KNN 50/50 solid solution is orthorhombic at room temperature and it undergoes a phase transition to tetragonal phase at 190 °C (O-T) and from tetragonal to cubic phase (T-C) at 400 °C (Curie temperature)<sup>14</sup>. The DSC cooling curve of undoped KNN reveals two sharp exo peaks with onsets at 188 °C and 405 °C, which correspond to the respective phase transitions. The phase transitions are reversible, exhibiting endothermic effects upon heating. Mg-doping decreases the (O-T) transition for 9 °C but it has no influence on the (T-C) transition. The effect of both Ca and Sr is quite similar: both transition temperatures are decreased, (O-T) for 15-17 °C and (T-C) for 7-8 °C. Note the sharpening of the (T-C) peak in the two doped samples. The Ba-doped KNN, which contains a noticeable amount of a secondary phase, exhibits similar, but markedly broader phase transitions as the undoped KNN sample.

The influence of Ca- and Sr-doping on the dielectric and piezoelectric response of KNN has been evaluated. Dielectric constant, losses and  $d_{33}$  constant of undoped KNN ceramics measured at 10 kHz are 450, 0,06 and 80 pC/N.

The dielectric constant and piezo  $d_{33}$  coefficient determined by Berlincourt piezo  $d_{33}$ -meter of Ca and Sr-doped KNN ceramics are about 500 and 95 pC/N, respectively, slightly higher than the values obtained for the undoped KNN.

## **Summary**

Earth-alkaline doping in the amount of 0.5 atom% influence on sinterability and functional response of KNN ceramics is studied. Mg, Ca and Sr ions are incorporated into the perovskite phase. We conclude that Ca and Sr occupy the A-sites of the perovskite lattice, promote densification, decrease the phase transition temperatures, namely from cubic to tetragonal and from tetragonal to cubic phase; and also slightly improve the functional response in

comparison to undoped KNN in the same manner. Mg ion, however, inhibits densification and has got only a minor effect on the phase transition temperatures relative to KNN. Even a low amount of Ba, namely 0.5 atom%, leads to the appearance of a noticeable amount of secondary phase(s).

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## Figure Captions

Figure 1: XRD spectra of KNN-based powders after the calcination.

\*: Al sample holder, #:diffraction peaks corresponding to secondary phase(s) in Ba-doped KNN.

Figure 2: XRD spectra of undoped and doped KNN ceramics sintered at 1115 °C, 2 hours.

The notation of the orthorhombic perovskite KNN phase was proposed by Stanek<sup>11</sup>.

Figure 3: SEM micrographs of the polished microstructures of the undoped and AE-doped KNN ceramics.

Figure 4: DSC cooling curves of the undoped and AE-doped KNN ceramics. The onset temperatures of the two exothermic peaks corresponding to cubic to tetragonal (in the 400 °C range) and tetragonal to orthorhombic phase transitions are denoted on the graph. The curves have been shifted for better clarity. The uncertainty of the analysis is  $\pm 0,3$  °C.

Table 1. Ionic radii and coordination numbers (CN) of selected cations <sup>9</sup>.

Cation	Ionic radius (nm)	CN
Na <sup>+</sup>	0.139	12
K <sup>+</sup>	0.164	12
Mg <sup>2+</sup>	0.072	6
Mg <sup>2+</sup>	*	12
Ca <sup>2+</sup>	0.134	12
Sr <sup>2+</sup>	0.144	12
Ba <sup>2+</sup>	0.161	12
Nb <sup>5+</sup>	0.064	6

\*: no data for CN 12

Table 2. Cell parameters, sintered density, dielectric constant and losses measured at 10 kHz and piezo  $d_{33}$  constant of undoped and AE-doped KNN ceramics sintered at 1115 °C for 2 hours. The theoretical density (TD) of KNN was used also for calculating the relative densities of doped ceramics.

Dopant	a [nm]	b [nm]	c [nm]	V [nm <sup>3</sup> ]	$\rho$ (gcm <sup>-3</sup> )	% TD	$\epsilon$	tan $\delta$	$d_{33}$ (pC/N)
-	0.4005(5)	0.3947(4)	0.4002(4)	0.0633(2)	4.26	94.4	450	0.06	80
Mg <sup>2+</sup>	0.3999(4)	0.3945(3)	0.3995(3)	0.0630(2)	4.11	91.2	-	-	-
Ca <sup>2+</sup>	0.3999(5)	0.3944(4)	0.4012(4)	0.0633(2)	4.23	93.8	495	0.12	95
Sr <sup>2+</sup>	0.4001(6)	0.3949(5)	0.4006(4)	0.0633(2)	4.33	96.0	500	0.04	95
Ba <sup>2+</sup>	-	-	-	-	4.24	94.1	-	-	-

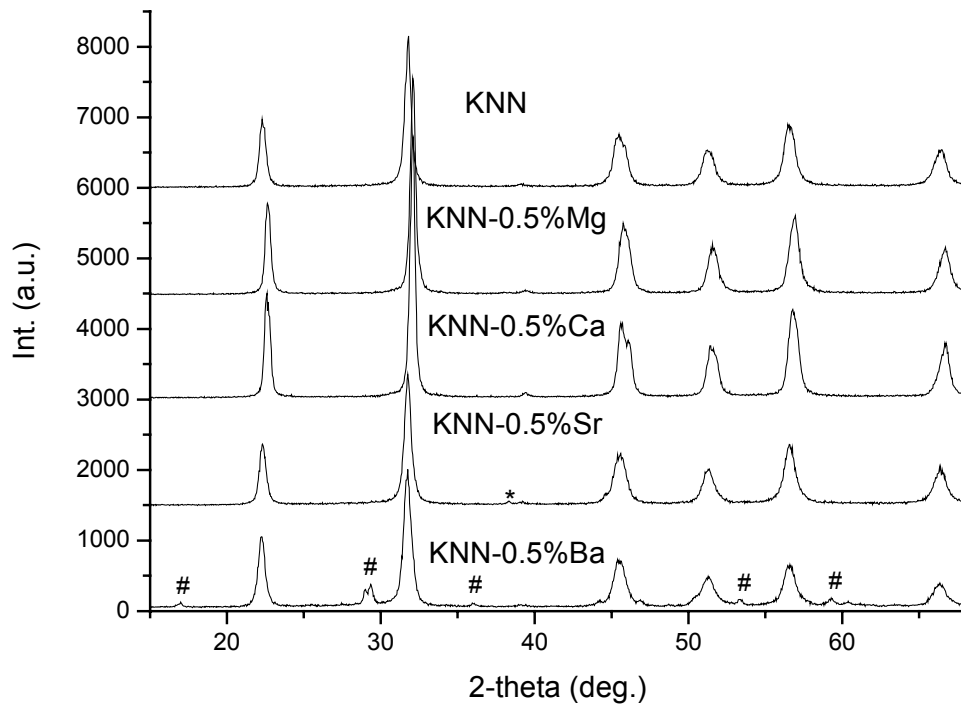


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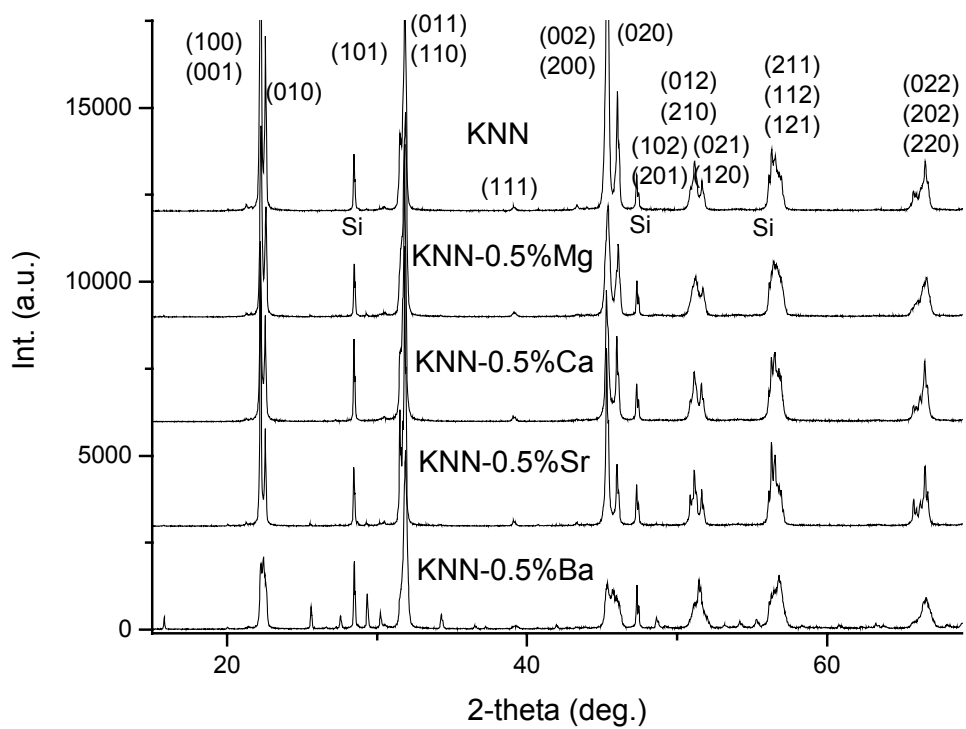


Figure 2: XRD spectra of undoped and doped KNN ceramics sintered at 1115 °C, 2 hours. The notation of the orthorhombic perovskite KNN phase was proposed by Stanek<sup>11</sup>.

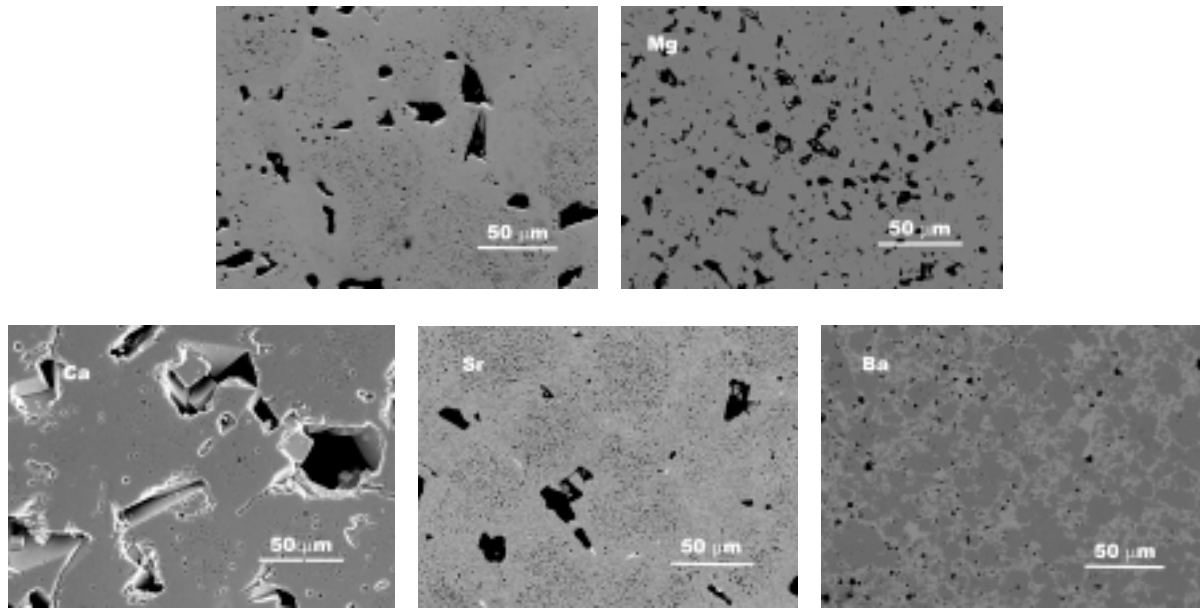


Figure 3: SEM micrographs of the polished microstructures of the undoped and AE-doped KNN ceramics.

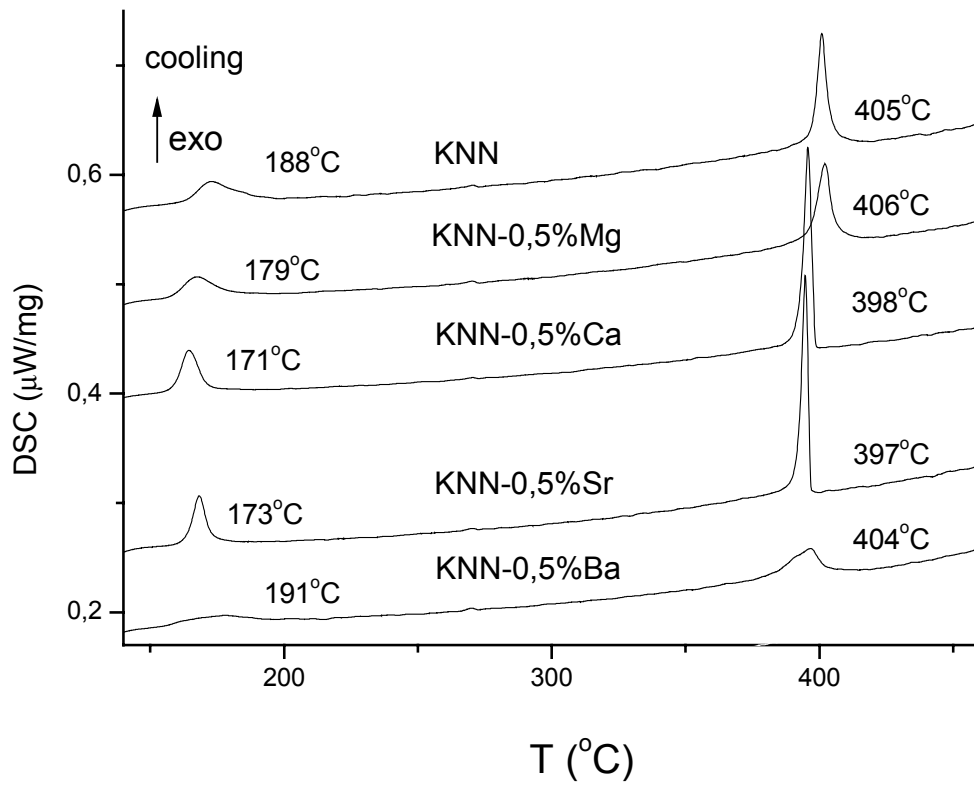


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