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Vapour pressure and mixing thermodynamic properties of the $KNbO_3$-$NaNbO_3$ system

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Abstract

Equilibrium vapour pressures of sodium and potassium over $K_xNa_{1-x}NbO_3$ solid solution within its whole compositional range at temperatures between 1173 K and 1303 K were determined by Knudsen Effusion Mass Spectrometry. It should be noted that the thermodynamic equilibrium between the condensed and the vapour phase could be established only after prolonged annealing (more than 10 h at 1263 K). The equilibrium vapour pressure of potassium over $K_{0.5}Na_{0.5}NbO_3$ (KNN) is a few times larger than that of sodium, i.e., $8\cdot10^{-3}$ Pa as compared to $3\cdot10^{-3}$ Pa at 1263 K. From the obtained results, the excess thermodynamic functions for the pseudo-binary $KNbO_3$-$NaNbO_3$ system were evaluated. The excess Gibbs energy was found positive, the excess enthalpy is close to zero, while the negative excess entropy indicates a partial ordering of alkaline ions in the solid solution. The comparison of the obtained results to the well-established lead-based piezoelectric systems revealed, that the vapour pressure of alkalis over the respective

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niobates at 1200 K is almost three orders of magnitude lower as compared to the values reported for lead oxide over $Pb(Zr,Ti)O_3$ (cf. refs. 16, 20).

1. Introduction

Piezoelectrics are technologically important materials, which enable coupling between mechanical and electrical signals and are therefore widely used in various electronic applications [1]. Lead-based perovskite materials, such as, $Pb(Zr_{1-x},Ti_x)O_3$ (PZT) or $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) are most widely used; however, these materials contain up to 70 wt. % lead, which represents a possible health and ecological hazard. The increased environmental awareness, supported by the restriction of use of hazardous substances [2], drives the search for new lead-free piezoelectric materials, that would replace the widely used lead-based piezoelectrics. Good ferroelectric and piezoelectric properties were observed in alkali-niobate based ceramics, including the $K_{0.5}Na_{0.5}NbO_3$ solid solution (KNN) [3]. Moreover, these materials enable the use of nickel electrodes - a large advantage over PZT, due to the significant reduction in processing cost [4].

Despite the large potential of KNN-based lead-free piezoelectric materials, the poor reproducibility of the functional properties still prevents their wide use in commercial applications [3, 5, 6]. The reasons for the observed variation of the properties are mostly related to difficult and poorly understood processing, originating from hygroscopicity of the starting compounds [7], different phase composition of the precursors [8], different diffusion rates of constituent ions resulting in local compositional inhomogeneities [9], and specific sintering mechanism [10]. Furthermore, presence of secondary alkali-poor phases and consequent degradation of functional properties has been attributed to loss of alkaline species upon sintering. In different studies loss of either sodium or potassium from the ceramic matrix was determined or assumed [11, 12], and according to our opinion such

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discrepancies could be due to different solid-state synthesis or sintering conditions, different stoichiometries of the studied materials, or even difficulties related to exact determination of the local chemical composition [13, 14]. According to our knowledge no data on vapour pressures of alkali species in the $KNbO_3$ – $NaNbO_3$ system have been reported. It should be recalled at this point that a few decades ago, a similar situation was encountered in the case of PZT ceramics. Seminal works of Holman and Fulrath [15], Härdtl and Rau [16], and Kingon [17] contributed to our present understanding and ability to control the vapour pressure of lead oxide during sintering of PZT within its whole compositional range.

Thus the aim of this work has been to measure the vapour pressure of both alkali metals over the whole compositional range from which the excess thermodynamic functions of mixing could be evaluated for the $KNbO_3$-$NaNbO_3$ pseudo-binary system. As in our previous study of the Na_2O-Nb_2O_5 system [18], Knudsen Effusion Mass Spectrometry (KEMS) was used. Finally, the obtained vapour pressures of alkalis over respective niobates are compared to the vapour pressures of bismuth and potassium over $Bi_{0.5}K_{0.5}TiO_3$ [19], and PbO over $Pb(Zr,Ti)O_3$ solid solution [16, 20].

Thermodynamic background

In a typical KEMS experiment, the sample is heated within an almost closed container (Knudsen cell) so that the thermodynamic equilibrium is established between gaseous and condensed phases. Molecules and/or atoms of the gas phase are let to effuse through the orifice into the evacuated surrounding, entering the ion source of the mass spectrometer. The as-formed ions are analyzed by their m/z (mass to charge) ratio and their abundance is measured by an appropriate detector.

The vapour pressure (p_j) of any species *(j)* within the Knudsen cell is proportional to the measured ion intensity (I_{ij}) of the ion *i* (counts per second in our case) originating

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from species *j* and the absolute temperature of the cell (*T*) according to Eq. (1) [21], where *K* is the instrumental sensitivity constant and σ_j is the ionisation cross section of species *j*. *K* can be determined *e.g*. by evaporation of a material with known vapour pressure (*e.g.* Ag) in a separate experiment.

$$p_j = \frac{KT}{\sigma_j} \cdot \sum_i I_{ij}^+ \tag{1}$$

In studies of binary systems Belton and Fruehan [22] as well as Neckel and Wagner [23] independently showed that it is possible to obtain the thermodynamic activities of both components without determining the absolute vapour pressures of the components just by measuring the ion intensity ratio of ions originating from the components over the complete compositional range. This in the present case means that one should measure the ion intensity ratio of ions originating from $NaNbO_3$ and $KNbO_3$. However, in recent KEMS study of $NaNbO_3$ [18] it was found that at elevated temperatures, the main gaseous species in equilibrium over the condensed phase were sodium atoms and oxygen molecules, as the result of the equilibrium decomposition Reaction (2), as follows:

$$4\ NaNbO_3(s) \Leftrightarrow Na_2Nb_4O_{11}(s) + 2\ Na(g) + 1/2\ O_2(g) \tag{2}$$

Similarly, potassium atoms and oxygen molecules could be anticipated to be the main gaseous components in the case of $KNbO_3$. It will be shown below, that it is possible to obtain the activities of both components, *i.e.*, $KNbO_3$ and $NaNbO_3$, also by measuring the K^+/Na^+ ion intensity ratio over the complete composition interval. In the case of $K_xNa_{1-x}NbO_3$ solid solution (ss) within the pseudo-binary $NaNbO_3$ - $KNbO_3$ system, both

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sodium and potassium take part in the following equilibrium exchange evaporation reaction:

$$\mathrm{NaNbO_3(ss) + K(g) \Leftrightarrow KNbO_3(ss) + Na(g)} \qquad (3)$$

The equilibrium constant (K_{eq}) of Reaction (3) is defined as

$$K_{\mathrm{eq}} = \frac{a_{\mathrm{KNbO_3(ss)}} \cdot \left(p_{\mathrm{Na(g)}} / p^{\mathrm{o}}\right)}{a_{\mathrm{NaNbO_3(ss)}} \cdot \left(p_{\mathrm{K(g)}} / p^{\mathrm{o}}\right)} \qquad (4)$$

where p^{o} = 1 bar denotes the standard pressure, while p and a denote the vapour pressure and activity, respectively. Therefore the ratio of the activities of the two components in the solid solution is related to the ratio of vapour pressures of sodium and potassium atoms in the vapour phase (Eq. (5)) as

$$\frac{a_{\mathrm{KNbO_3(ss)}}}{a_{\mathrm{NaNbO_3(ss)}}} = \frac{p_{\mathrm{K(g)}}}{p_{\mathrm{Na(g)}}} \cdot K_{\mathrm{eq}} \qquad (5)$$

Applying the relationship between the vapour pressure and ion intensity presented in Eq. (1), Eq. (5) turns to:

$$\frac{a_{\mathrm{KNbO_3(ss)}}}{a_{\mathrm{NaNbO_3(ss)}}} = \frac{I_{\mathrm{K^+(g)}}}{I_{\mathrm{Na^+(g)}}} \cdot \frac{\sigma_{\mathrm{Na(g)}}}{\sigma_{\mathrm{K(g)}}} K_{\mathrm{eq}} \qquad (6)$$

The corresponding equation for the ratio of the activity coefficients is as follows:

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$$\frac{\gamma_{\mathrm{KNbO_3(ss)}}}{\gamma_{\mathrm{NaNbO_3(ss)}}}=\frac{I_{\mathrm{K^+(g)}}}{I_{\mathrm{Na^+(g)}}}\cdot\frac{\sigma_{\mathrm{Na(g)}}}{\sigma_{\mathrm{K(g)}}}\frac{X_{\mathrm{NaNbO_3(ss)}}}{X_{\mathrm{KNbO_3(ss)}}}K_{\mathrm{eq}} \tag{7}$$

where γ and X denote the activity coefficient and the mole fraction, respectively.

The activity of $NaNbO_3$ using the well-known Gibbs-Duhem relationship can be obtained as follows [24]:

$$\ln a_{\mathrm{NaNbO_3(ss)}}=\int_{X_{\mathrm{KNbO_3(ss)}}=0}^{X_{\mathrm{KNbO_3(ss)}}} X_{\mathrm{KNbO_3(ss)}}\,d\ln\left[\frac{a_{\mathrm{KNbO_3(ss)}}}{a_{\mathrm{NaNbO_3(ss)}}}\right] \tag{8}$$

The corresponding equation for the activity coefficients is as follows:

$$\ln \gamma_{\mathrm{NaNbO_3(ss)}}=\int_{X_{\mathrm{KNbO_3(ss)}}=0}^{X_{\mathrm{KNbO_3(ss)}}} X_{\mathrm{KNbO_3(ss)}}\,d\ln\left[\frac{\gamma_{\mathrm{KNbO_3(ss)}}}{\gamma_{\mathrm{NaNbO_3(ss)}}}\right] \tag{9}$$

The change of the logarithm of the ratio of the activity coefficients by changing the composition can be obtained from Eq. (7) as:

$$d\ln\left[\frac{\gamma_{\mathrm{KNbO_3(ss)}}}{\gamma_{\mathrm{NaNbO_3(ss)}}}\right]=d\ln\left[\frac{I_{\mathrm{K^+(g)}}}{I_{\mathrm{Na^+(g)}}}\right]-d\ln\left[\frac{X_{\mathrm{KNbO_3(ss)}}}{X_{\mathrm{NaNbO_3(ss)}}}\right]=d\ln\left[\frac{I_{\mathrm{K^+(g)}}X_{\mathrm{NaNbO_3(ss)}}}{I_{\mathrm{Na^+(g)}}X_{\mathrm{KNbO_3(ss)}}}\right] \tag{10}$$

since the other terms (ionisation cross sections, equilibrium constant) are constant, *i.e.*, they do not change with the composition. Therefore the final equation for the determination of the activity coefficient of $NaNbO_3$ is as follows:

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$$\ln \gamma_{\mathrm{NaNbO_3(ss)}} = \int_{X_{\mathrm{KNbO_3(ss)}}=0}^{X_{\mathrm{KNbO_3(ss)}}} X_{\mathrm{KNbO_3(ss)}}\, d\ln\left[\frac{I_{\mathrm{K^+(g)}} X_{\mathrm{NaNbO_3(ss)}}}{I_{\mathrm{Na^+(g)}} X_{\mathrm{KNbO_3(ss)}}}\right] \qquad (11)$$

Analogous formulas hold for $KNbO_3$.

It should be notified at this point, that the ion intensities of Na^+ and K^+ linearly correlate with the partial pressures of Na(g) and K(g) (see Eq. (1)) which, in turn, correlate with the activities of Na_2O and K_2O in a multi-oxide (in our case ternary oxide) system as follows [18]:

$$a_{\mathrm{Na_2O}} = \left(\frac{p_{\mathrm{Na(g)}}}{p^*_{\mathrm{Na(g)}}}\right)^{\frac{5}{2}} \qquad a_{\mathrm{K_2O}} = \left(\frac{p_{\mathrm{K(g)}}}{p^*_{\mathrm{K(g)}}}\right)^{\frac{5}{2}} \qquad (12)$$

Here p^* denotes the vapour pressures over the pure condensed alkali oxides. Nevertheless, the purpose of this study was the determination of the activities of $NaNbO_3$ and $KNbO_3$ in the $K_xNa_{1-x}NbO_3$ pseudo-binary system, rather than the determination of the activities of Na_2O, K_2O and Nb_2O_5 in the pseudo-ternary system along constant mole fraction (0.5) of Nb_2O_5. Both purposes could be performed by measuring the ion intensities of Na^+ and K^+ but the object of interest was the pseudo-binary system.

2. Materials and methods

Materials and sample preparation

The starting powder mixtures with different K/Na molar ratios (10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10) were prepared according to the stoichiometric formula $K_xNa_{1-x}NbO_3$ from high purity Nb_2O_5 (99.9 %, Sigma-Aldrich, Taufkirchen, Germany), K_2CO_3 (anhydrous 99.9 %, Chempur, Karlsruhe, Germany) and

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Na_2CO_3 (anhydrous 99.9 %, Chempur, Karlsruhe, Germany). Hereafter the samples will be further referred to by their K/Na molar ratio, *e.g.*, “KNN50/50”. Both carbonates were high-energy milled prior to mixing in a planetary ball mill for 4 h (Pulverisette 4 Vario-Mill, Fritsch, Idar-Oberstein, Germany) using a tungsten carbide vial and balls. The starting compounds were weighted under dry atmosphere and homogenized in a planetary ball mill for 4 h using zirconia vial and balls and acetone as a liquid medium. Finally the powder mixtures were dried and kept in closed vials for further use.

The X-ray diffractograms (XRD) were recorded using the PANalytical X’Pert PRO diffractometer with CuKα_1 radiation and a graphite monochromator (PANalytical B.V., Almelo, the Netherlands). The data were collected in the 2θ range from 10° to 60° with a step of 0.034°/100 s.

KEMS experiments

A 60-degree magnetic low-resolution mass spectrometer with a modified Nier-type ion source was used. A detailed description of the apparatus can be found elsewhere [18]. In preliminary experiments, 330 mg of alkali carbonates and niobium oxide mixture with 50/50 Na-to-K molar ratio (KNN50/50) was loaded into the platinum Knudsen cell with an orifice diameter of 0.05 mm. The sample was then calcined for 12 h at 950 °C in open air. The purpose of such small orifice was to minimize any possible loss of alkali elements from the powder, still letting the carbon dioxide to escape. As a result of such arrangement, $K_{0.5}Na_{0.5}NbO_3$ (KNN) was formed under predominant CO_2 atmosphere. After fast cooling, a portion (204 mg) of such KNN sample was loaded in the Pt Knudsen cell with the orifice diameter of 0.1 cm, placed into the evaporator of the mass spectrometer and evacuated. When the vacuum reached 10^{-6} Torr, the sample was heated at a rate of 10 K min^{-1} until the Na^+ and K^+ ions could be detected at about 800 °C. The temperature

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was then rapidly increased to 890 °C and kept constant for 21 h. The temperature was subsequently increased again to 990 °C and kept constant for additional 24 h.

In the second series of KEMS experiments, the activities of the KNN samples with different KN/NN molar ratios were determined in the Knudsen cell with the 1 mm orifice. About 200 mg of carbonate-oxide mixture in the required stoichiometric ratio were loosely pressed into an alumina cell and annealed at 950 °C for 10 h in open air. The Knudsen cell with the sample was immediately transferred into the evaporator, evacuated, and heated to 990°C at the rate of 10 K min^{-1}. When the final temperature was reached, the ion intensities I_{K^+} and I_{Na^+} were monitored until their values became constant. This usually took about 10 h, much faster than in the preliminary experiment. During this equilibration time some alkalis were also lost, slightly altering the stoichiometry; however, it was assessed to have no significant effect on final results. The temperature was then increased to 1030 °C at which the measurement was started. The data were collected at each 10 °C down to 900 °C. Each experimental point was collected for 10 s or 60 s when the counting rate became less than 100 s^{-1}.

3. Results and discussion

In the preliminary KEMS experiment the KNN50/50 specimen was loaded in a Pt Knudsen cell with the orifice diameter of 0.09 mm, and heated at 890 °C and 990 °C. The measured intensities of K^+ and Na^+ ions are presented in Figure 1, while the full set of data is given in the supplemental material (Table S-I). The time dependencies of the pressures of both alkalis clearly indicate that the thermodynamic equilibrium of the system was not reached during the solid state synthesis at 950 °C for 12 h in the CO_2–enriched atmosphere, related to the extremely fine orifice of the cell.

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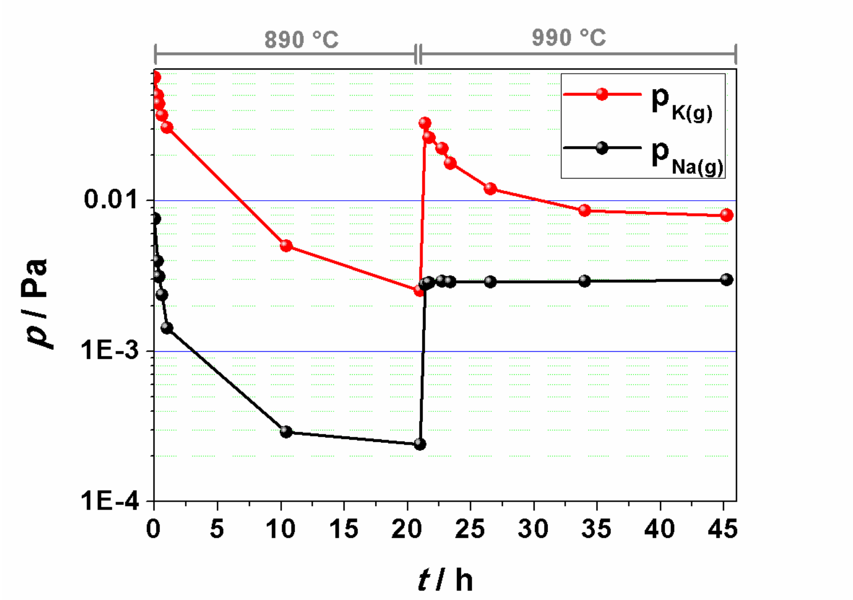

Figure 1. Time-temperature dependence of sodium and potassium vapour pressures over $K_{0.5}Na_{0.5}NbO_3$, previously prepared by calcination of the oxide-carbonate mixture at 950°C, 12 h. The values of vapour pressures were calculated from the measured intensities according to Eq. (1).

Evidently, the activity of Na_2O attains, or is close to the equilibrium upon heating for 21 h at 890 °C, while the activity of K_2O keeps decreasing upon additional heating step for 23 h at 990 °C (see Figure 1), until the thermodynamic equilibrium is finally reached.

The XRD patterns of the KNN50/50 samples before (in a Pt-cell) and after the KEMS experiment are depicted in Figure 2, together with the pattern of a KNN50/50 sample, conventionally calcined at 950 °C in an Al_2O_3 crucible, which is added for comparison. The latter crystallizes in the perovskite phase, in agreement with Ref. [25]. In the sample calcined in the Pt-cell the perovskite phase coexists with traces of Nb_2O_5 and traces of $(K,Na)_6Nb_{10.88}O_{30}$. This niobium-rich phase can be formed either at too low thermal budget [26], or as a result of excessive alkali-loss during prolonged heating at high temperatures [9]. In the present case its presence could be related to the CO_2–enriched atmosphere during heating, which presumably shifts the equilibrium of the KNN synthesis

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reaction towards the reagents side. The pattern of the sample after KEMS analysis, revealed the presence of the perovskite and $(K,Na)_6Nb_{10.88}O_{30}$ phases, while reflections of Nb_2O_5 were not detected. This result underlines the importance of the careful control of the calcination conditions, which should enable removal of the gaseous reaction product (in this case CO_2). This can be achieved by selecting a low-enough powder/container volume ratio thus allowing the gas exchange between the container and surrounding atmosphere.

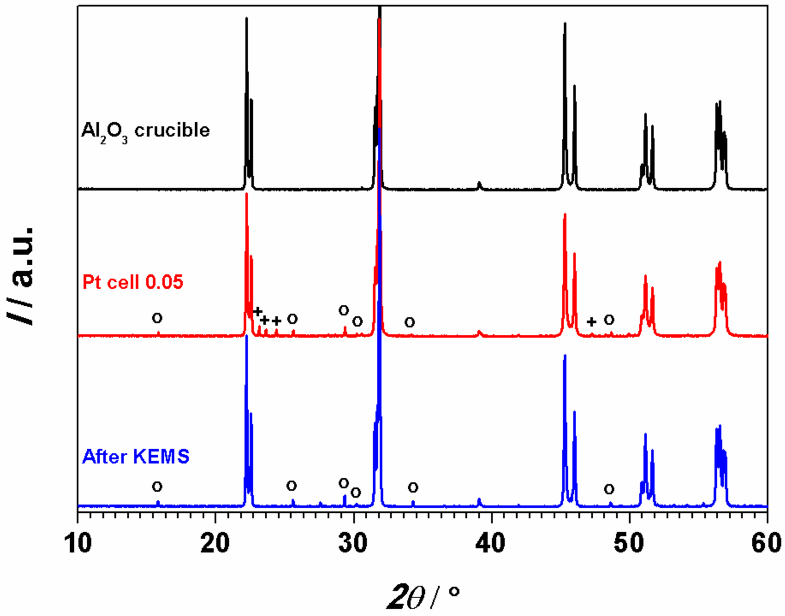

Figure 2. X-ray diffraction patterns of KNN powders, calcined under different conditions: conventional calcination in an Al_2O_3 crucible, calcination in a Pt Knudsen cell with a 0.05 mm orifice, and after subsequent KEMS measurement (+ traces of Nb_2O_5; o identified as $(K,Na)_6Nb_{10.88}O_{30}$).

During this experiment, which lasted 45 h, a certain amount of alkalis evaporated from the sample. The loss of sodium and potassium from the Knudsen cell was assessed using the Hertz-Knudsen-Langmuir equation (Eq. (13)) [21].

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$$\left(\frac{dm_i}{dt}\right) = 0.44 \cdot A \cdot p_i \cdot \sqrt{\frac{M_i}{T}} \tag{13}$$

where $\left(\frac{dm_i}{dt}\right)$ is the mass flux of the effusing species i in mg/sec, *A* is orifice area in cm^2, p_i is the pressure of species i in Pa, M_i is the molecular mass of species *i* and *T* is the absolute temperature. The total mass losses of sodium and potassium were obtained by integration of the pressure-time data depicted in Table S-I. The conversion of ion intensity (in s^{-1}) to pressure (columns 5 and 6) was performed using Eq. (1).

As a result it was obtained that 1.16 mg of potassium and 0.14 mg of sodium evaporated from the initial 204 mg of KNN50/50 sample during the KEMS experiment – this represents almost 5 mole % of the total potassium, while the loss of sodium was about 10 times lower. Quite surprisingly, in spite of such massive loss of potassium, neither additional secondary phases were detected in the residual material nor a change in the relative amount of the $(K,Na)_6Nb_{10.88}O_{30}$ phase could be observed (see Figure 2). Certainly, the above assessment should not be correlated with the loss of alkalis during conventional solid-state synthesis of KNN, which is conducted in air atmosphere where the rate of alkali evaporation is hindered both kinetically and thermodynamically. In several auxiliary experiments it was observed that the evaporation rate in air is about fifty times lower than in vacuum.

Measurements of activity of $KNbO_3$ and $NaNbO_3$ in KNN solid solutions

In the second series of KEMS experiments, the larger orifice of the Knudsen cell allowed better interchange of CO_2 with air and in this case the as-synthesized KNN solid solutions consisted of pure perovskite phase only (XRD patterns not shown).

The data for a selected analysis of the KNN20/80 sample are shown in Figure 3, while the raw data can be found in the supplemental material (Table S-II).

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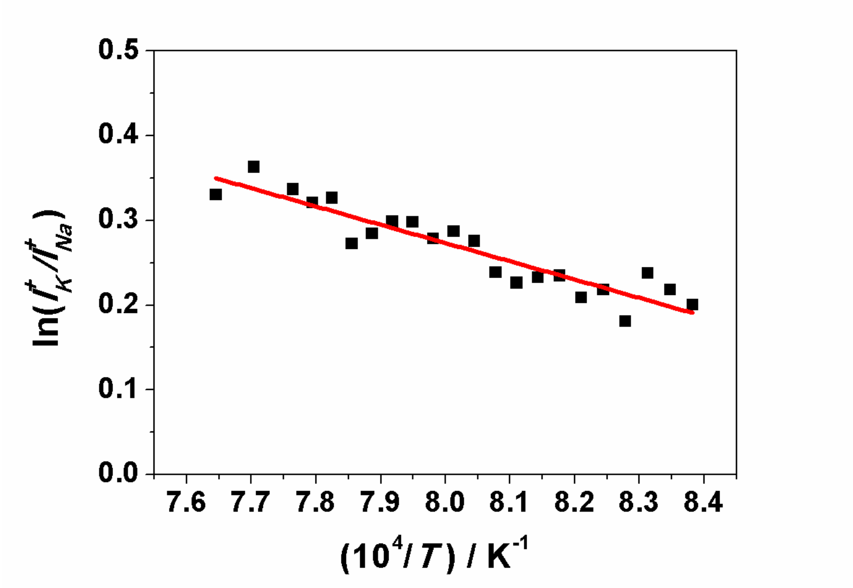

Figure 3. $\ln(I_{\mathrm{K}^+}/I_{\mathrm{Na}^+})$ *vs.* (10^4/(*T*/K)) for a selected analysis of the KNN20/80 sample. The line represents the linear fit.

The resulting slope and the intercept for this particular measurement are -2157 ± 200 and 1.999 ± 0.7, respectively. Several similar runs were performed for each composition starting from KNN10/90 to KNN90/10. The complete results for the nine studied compositions are collected in Table I, where the necessary data to evaluate the excess thermodynamic functions/properties of mixing of the studied binary system are included. The parameters *A* and *B* determine the $I_{\mathrm{K}^+}/I_{\mathrm{Na}^+}$ ion intensity ratio at the temperature *T* according to Eq. (14) as follows:

$$\ln(I_{\mathrm{K}^+}/I_{\mathrm{Na}^+}) = A/T + B \tag{14}$$

In order to calculate the activity coefficients as described by Eq. (11), it should be rewritten in the trapezian summation form as:

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$$\ln \gamma_{\mathrm{NaNbO_3\,(ss)}_{i+1}} = \sum_{i=0}^{i} \left(\frac{X_{\mathrm{KNbO_3\,(ss)}_{i+1}} + X_{\mathrm{KNbO_3\,(ss)}_{i}}}{2} \right) \cdot \left(\ln\left(\frac{RI_{i+1}}{RI_i} \right) - \ln\left(\frac{RX_{i+1}}{RX_i} \right) \right) \tag{15}$$

where *RX* and *RI* represent the ratio of mole fractions ($X_{\mathrm{KNbO_3\,(ss)}} / X_{\mathrm{NaNbO_3\,(ss)}}$) and the ratio of the ion intensities ($I_{\mathrm{K^+}} / I_{\mathrm{Na^+}}$), respectively. The subscripts *i* and *i*+1 denote the two subsequent (neighbouring) measured compositions. An analogous expression holds also for $KNbO_3$.

Table I. Mean values of the *A* and *B* parameters for the investigated compositions, representing the slope and the intercept data of particular $I_{\mathrm{K^+}} / I_{\mathrm{Na^+}}$ *vs.* (1/*T*) lines, obtained from the KEMS measurements. Values in brackets are standard deviations.

comp.	No of runs	–*A*	*B*
10/90	5	2098(±148)	1.66(±0.20)
20/80	5	2167(±409)	2.19(±0.43)
30/70	6	2134(±566)	2.60(±0.46)
40/60	6	1998(±200)	2.87(±0.23)
50/50	3	1968(±275)	3.13(±0.30)
60/40	4	1994(±235)	3.52(±0.30)
70/30	4	2067(±300)	3.79(±0.25)
80/20	3	2182(±453)	4.16(±0.28)
90/10	5	1953(±492)	4.38(±0.49)

The activities of both $KNbO_3$ and $NaNbO_3$, were extracted from both activity coefficients, as shown in Figure 4. Evidently, the system exhibits a positive deviation from Raoult’s law.

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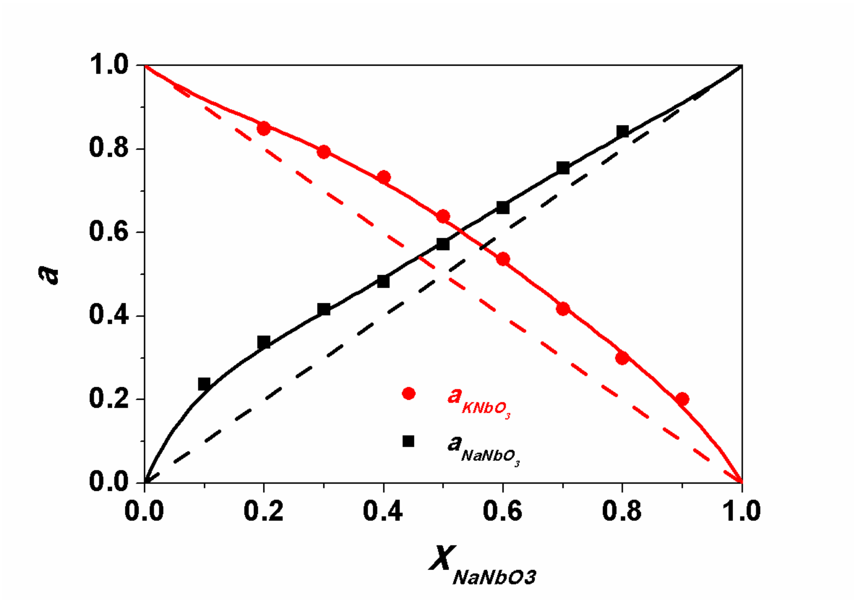

Figure 4. Activities of $NaNbO_3$ and $KNbO_3$ in (K,Na)NbO_3 solid solution system at 950 °C. The symbols represent experimental points, the solid lines were obtained by fitting the experimental data to Redlich-Kister sub-regular solution model. Dashed lines: ideal mixture expressed by Raoult's law.

Furthermore, the excess integral molar thermodynamic functions (G^E, H^E and S^E) can generally be fitted to the Redlich-Kister (R-K) sub-regular mixture model [27]. Accordingly, the excess integral molar Gibbs energy, for the $KNbO_3$ – $NaNbO_3$ system, can be expressed as:

$$G^E = X_{NaNbO_3(ss)} \cdot X_{KNbO_3(ss)} \cdot \left[C0 + C1 \cdot \left(X_{NaNbO_3(ss)} - X_{KNbO_3(ss)}\right) + C2 \cdot \left(X_{NaNbO_3(ss)} - X_{KNbO_3(ss)}\right)^2\right] \quad (16)$$

where *C0*, *C1* and *C2* represent the R-K binary interaction parameters and *X* represents mole fractions of the components. The parameters can be evaluated by solving a set of linear equations (seven in the present case):

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$$\begin{bmatrix} XNa_1 \cdot XK_1 & XNa_1 \cdot XK_1 \cdot (XNa_1 - XK_1) & XNa_1 \cdot XK_1 \cdot (XNa_1 - XK_1)^2 \\ XNa_2 \cdot XK_2 & XNa_2 \cdot XK_2 \cdot (XNa_2 - XK_2) & XNa_2 \cdot XK_2 \cdot (XNa_2 - XK_2)^2 \\ \vdots & \vdots & \vdots \\ XNa_7 \cdot XK_7 & XNa_7 \cdot XK_7 \cdot (XNa_7 - XK_7) & XNa_7 \cdot XK_7 \cdot (XNa_7 - XK_7)^2 \end{bmatrix} \text{x} \begin{bmatrix} C0 \\ C1 \\ \vdots \\ C7 \end{bmatrix} = \begin{bmatrix} Gex_1 \\ Gex_2 \\ \vdots \\ Gex_7 \end{bmatrix} \quad (17)$$

In Eq. (17) *Gex* denotes the seven experimental values of the excess Gibbs energy obtained from activity coefficients and, *XNa* as well as *XK* in matrix *M* denote the mole fractions of $NaNbO_3$ and $KNbO_3$, respectively.

The resulting parameters (*C0*, *C1* and *C2*) are temperature-dependent and can be expressed as: $C0 = 6.65 \cdot T - 450$, $C1 = -1.07 \cdot T - 527$ and $C2 = 2.53 \cdot T - 219$. Thus inserting the temperature dependence into Eq. (16) it follows:

$$G^{\mathrm{E}} = X_{\mathrm{NaNbO_3}} \cdot X_{\mathrm{KNbO_3}} \cdot [(6.65 \cdot T - 450) + (-1.07 \cdot T - 527) \cdot (X_{\mathrm{NaNbO_3}} - X_{\mathrm{KNbO_3}}) + \\ + (2.53 \cdot T - 219) \cdot (X_{\mathrm{NaNbO_3}} - X_{\mathrm{KNbO_3}})^2] \quad (18)$$

Furthermore, the derivative of $\left(\dfrac{G^{\mathrm{E}}}{T}\right)$ with respect to temperature provides the excess enthalpy according to Eq. (19) as follows

$$H^{\mathrm{E}} = -T^2 \left[\frac{\partial \left(G^{\mathrm{E}} / T \right)}{\partial T} \right] \quad (19)$$

Finally, the excess entropy is obtained as:

$$S^{\mathrm{E}} = \frac{H^{\mathrm{E}} - G^{\mathrm{E}}}{T} \quad (20)$$

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The obtained integral excess thermodynamic properties as a function of the composition at 950 °C are presented in Figure 5.

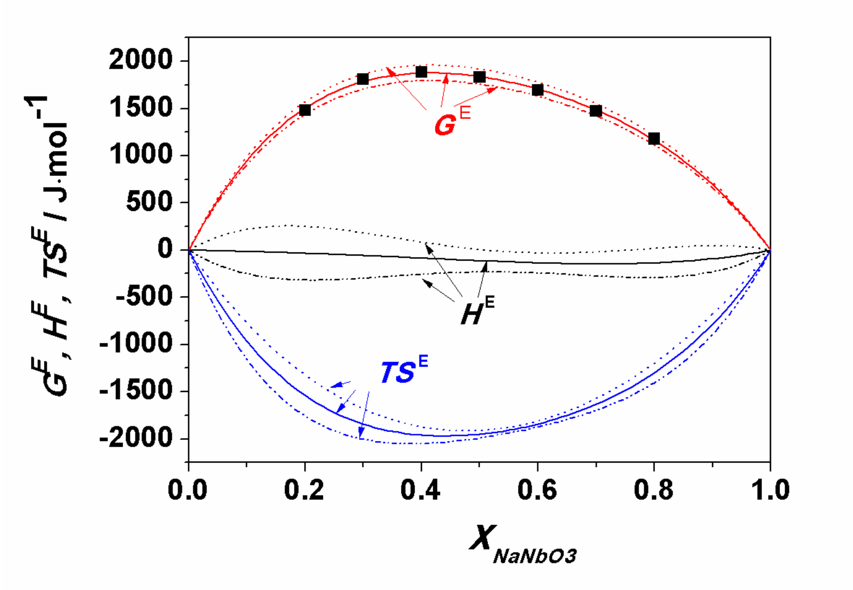

Figure 5. Excess integral functions in (K,Na)NbO_3 solid solution system at 950 °C. Square points represent the experimental data obtained by Gibbs-Duhem integration. Also shown are uncertainties calculated from uncertainties of parameters *A* and *B*, also depicted in Table I.

It is interesting to note that the system exhibits a positive deviation from Raoult's law with the negative excess entropy while the excess enthalpy is very low (close to zero). This could be also predicted directly from observing the values of parameters "*A*" depicted in Table I. A great effort was undertaken in order to detect the heat effect directly, using the high temperature differential scanning calorimetry (DSC) in order to compare the heat values obtained by KEMS. Nevertheless, no heat effect was detected by DSC. This could be due to a rather low heat effect as obtained by KEMS on one hand and to a relatively low rate of mixing reaction on the other. Namely, previous studies have shown that the synthesis of KNN50/50 from the binaries required a larger thermal budget (higher

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temperatures and extended heating times) in order to obtain a homogeneous solid solution [7, 25, 28] as compared to the synthesis from the carbonate-oxide mixture.

Since the excess enthalpy is negligible as compared to excess Gibbs energy, the latter arises mainly from the excess entropy as $G^{\mathrm{E}} \approx -TS^{\mathrm{E}}$. A relatively large negative value suggests that a partial ordering may occur during mixing. In other words, during mixing of $NaNbO_3$(s) and $KNbO_3$(s) the Na^+ and K^+ ions are not distributed randomly but should be partly occupying certain lattice sites. Other systems having negative excess entropies exhibit also some kind of ordering, *e.g.*, formation of associates in a melt, see Fraser *et al.* [29]. The paper is one of the numerous investigations of molten mixed alkali feldspars, where KEMS measurement of K^+/Na^+ provided information on thermodynamics of mixing. However, for solid solution systems such information is sparse. To our knowledge, no work regarding mixing thermodynamics of KNN has been published yet, despite of its potential to replace PZT. For the latter the G^E of mixing at 1373 K was determined by Jacob and Rannesh as +2 kJ/mole with maximum at the $PbZrO_3$ rich side [30]. It seems that both systems reveal similar behaviour from the G^E point of view. Mixing enthalpy of PZT was previously reported to be about +10 kJ/mole, as measured by Rane *et al.* using drop solution calorimetry [31]. In this case a large difference between G^E and H^E of mixing seems to be unrealistic from the S^E point of view. This therefore raises the question whether or not the drop solution method would be appropriate to confirm small heat effect of mixing found in the present work.

Comparison of vapour pressures of volatile species over selected perovskites

The obtained vapour pressures of potassium and sodium [18] over respective oxides and niobates were compared to the vapour pressure of PbO over pure PbO and $Pb(Zr,Ti)O_3$ solid solution, using the data reported in the literature [16, 20]. It should be noted that in contrast to alkalis, which exist in the vapour phase in atomic form, cf. Eq. 2, in the

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case of lead oxide and PZT, the vapour phase consists predominantly of monomeric lead oxide (PbO) and to a much lesser amount of lead (Pb) and dimeric lead oxide (Pb_2O_2). For sake of simplicity, this total vapour phase is in further text described as 'lead oxide'. Thus in the calculation an average molar mass of the vapour phase was implemented, cf. [20, 32]. The results for the temperature range 900 – 1200 K are presented in Figure 6. As described earlier in the paper, the vapour pressure of potassium over K_2O in the temperature range 900 – 1200 K is more than an order of magnitude higher than that of sodium over Na_2O, reaching the value of about $1{\cdot}10^2$ Pa for potassium at 1200 K. The vapour pressures of potassium and sodium over respective niobates are more than five orders of magnitude lower, $\sim 2{\cdot}10^{-3}$ Pa and $\sim 6{\cdot}10^{-4}$ Pa at 1200 K, respectively. Interestingly, the vapour pressure of lead oxide over condensed lead oxide is only slightly below the sodium over Na_2O curve, ~10 Pa at 1200 K, while the vapour pressure of lead oxide over the PZT solid solution is one order of magnitude lower, ~1 Pa at 1200 K.

In addition, the results are compared to the vapour pressures of bismuth and potassium over $Bi_{0.5}K_{0.5}TiO_3$ (BKT) reported in [19]. BKT was selected as a representative of the second largest group of lead-free piezoelectrics, *i.e.* the Bi-based materials [3]. The vapour pressure of bismuth over BKT at 1200 K is ~1 Pa and is very close to the pressure of lead-oxide vapour over PZT, while the vapour pressure of potassium over BKT is almost two orders of magnitude lower.

Based on the comparison presented above it can be concluded, that the vapour pressures of the volatile species during the high-temperature processing (calcination, sintering) of the PZT- and Bi-based piezoelectrics are orders of magnitude higher than the vapour pressures of alkalis in KNN-based systems.

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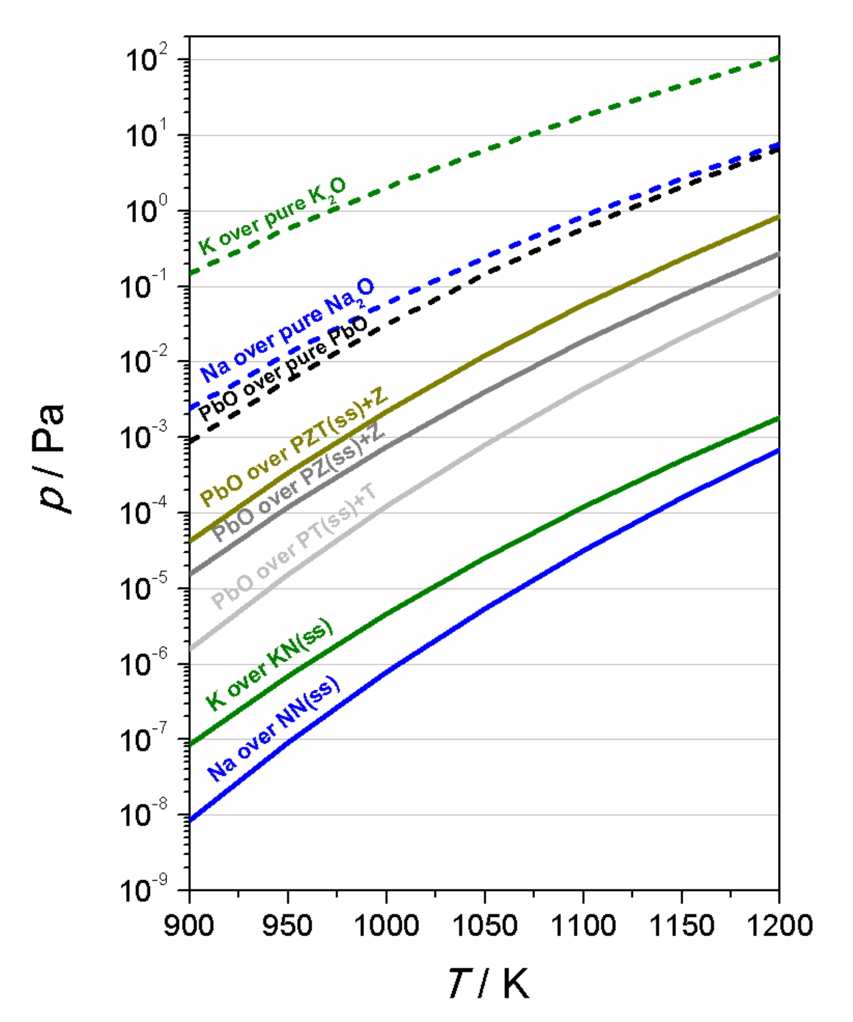

Figure 6. Vapour pressures of potassium (this work) and sodium[18] over respective oxides and niobates, of lead oxide over $PbTiO_3$+TiO_2 (PT+T), $PbZrO_3$+ZrO_2 (PZ+Z), $Pb(Zr_{0.5}Ti_{0.5})O_3$+ZrO_2 (PZTss+Z)[16, 20], and of bismuth and potassium over $Bi_{0.5}K_{0.5}TiO_3$ (BKT) [19].

4. Conclusions

Equilibrium vapour pressures of sodium and potassium over $K_xNa_{1-x}NbO_3$ solid solution within its whole compositional range at temperatures between 1173 K and 1303 K were determined by Knudsen Effusion Mass Spectrometry. The main gaseous species are alkaline atoms and oxygen molecules. The vapour pressure of potassium over $(K_{0.5}Na_{0.5}NbO_3)_{ss}$ is a few times higher as the vapour pressure of sodium. The

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thermodynamic equilibrium between the gaseous and condensed phase could be attained only after prolonged annealing (at least 10 h at 1263 K).

The ratio of the alkali ion intensities proved to be suitable for the determination of the activities of $NaNbO_3$ and $KNbO_3$ in solid solution using Gibbs-Duhem integration. The system exhibits a positive deviation from Raoult's law. The obtained negative excess entropy indicates that the alkalis are partially ordered in $((K_xNa_{1-x})NbO_3)_{ss}$.

The vapour pressures of alkalis over potassium and sodium niobate are almost three orders of magnitude lower than the vapour pressure of lead oxide over PZT or bismuth over BKT at 1200 K. Under the investigated experimental conditions there is no significant interaction between $NaNbO_3$ and $KNbO_3$.

5. Acknowledgements

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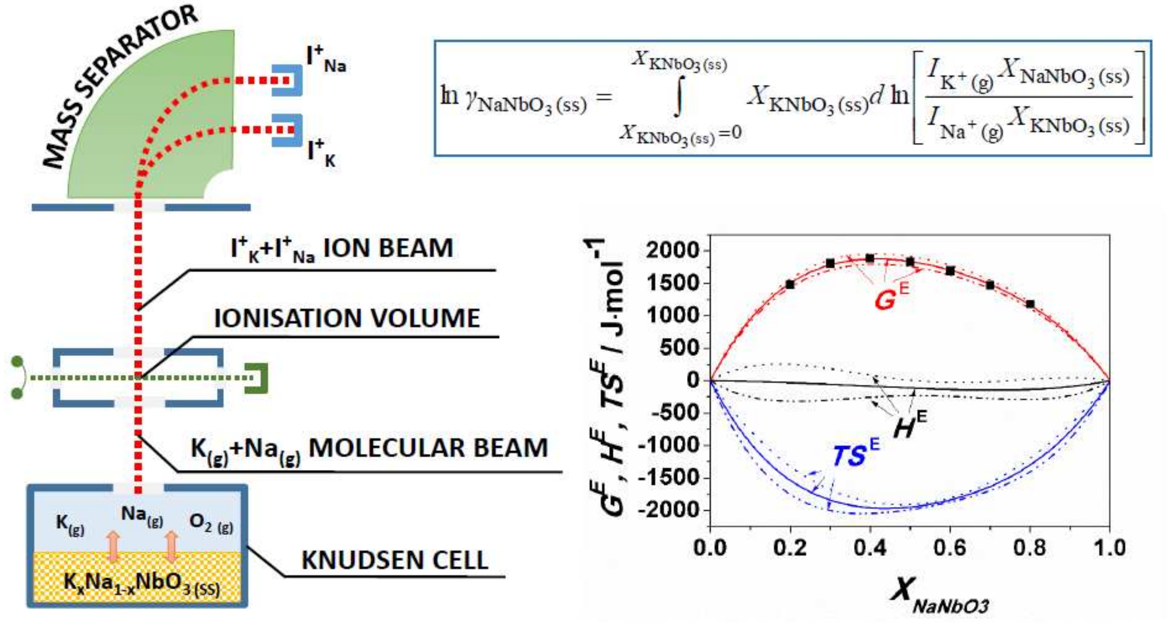
Abstract graphic



$$\ln \gamma_{NaNbO_3(ss)} = \int_{X_{KNbO_3(ss)}=0}^{X_{KNbO_3(ss)}} X_{KNbO_3(ss)}\, d \ln\left[\frac{I_{K^+(g)}\, X_{NaNbO_3(ss)}}{I_{Na^+(g)}\, X_{KNbO_3(ss)}}\right]$$

The analytical description of excess functions was made possible using more advanced treatment of experimental data with respect to literature.

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