Thermodynamic Vaporization Studies on Mn-doped Sodium Niobate

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Abstract

Thermodynamic studies of a Mn-doped single crystal sodium niobate ($NaNbO_3$:*x*Mn) under equilibrium conditions by the method of Knudsen Effusion Mass Spectrometry (KEMS) were conducted in the temperature range 1220 – 1500 K. The vaporization of pure Na_2O(c) as a reference was investigated at temperatures of 810 – 1090 K. Thermodynamic quantities of sublimation enthalpy, Gibb's energy for reactions, entropy, and activity was derived from the partial pressures of gaseous Na and O_2 over the sodium niobate and pure sodium oxide reference samples. The sublimation enthalpy of Na from nominal $NaNbO_3$:0.1%Mn at $T = 1350$ K was $\Delta_{sub}H^0_{1350\,K}(Na) = (348 \pm 5)$ kJ mol^{-1} The enthalpy and the entropy values were calculated from the vaporization studies. Deduced from empirical and experimental approaches, the heat of reaction $\Delta_r H^0_{298}(NaNbO_3{:}\,0.1\%Mn(c)) = -(75 \pm 7)$ kJ mol^{-1} and the heat of formation $\Delta_f H^0_{298}(NaNbO_3{:}\,0.1\%Mn(c)) = -(1242 \pm 7)$ kJ mol^{-1}was determined. The thermodynamic activity of Na in sodium niobate was temperature-dependent, and at a temperature of 1200 K, $a = 3.2 \cdot 10^{-2}$ for nominal $NaNbO_3$: 0.1%Mn(c). All collected values are given inside the article.

Keywords:

Mn-doped sodium niobate; thermodynamic data; Knudsen effusion mass spectrometry, partial pressure

Introduction

Compounds with functional properties like ferroelectric lead titanate and antiferroelectric sodium niobate have reached considerable interest in recent years. The quite high lead content in lead titanate leads to environmental concerns and a demand for lead-free materials (Shrout et al. [1]).

In particular, the electrical and physical properties such as their dielectric permittivity, temperature stability, high sound velocity, and low density have given them attractive characteristics for use in sensors, attenuators, actuators, and solid-state memories (Näfe *et al.* [2], Xu *et al.* [3]). The ferroelectric sensors demand materials with high stability, both in temperature and time.

The high-temperature thermodynamic properties of sodium niobate crystals have been studied in a paper by Kobertz *et al.* [4]. The manganese-doped material was studied here in this work firstly from the view of the vapor phase.

The study of the vapor phase of Mn-doped $NaNbO_3$(c) was related to Knudsen effusion mass spectrometry (KEMS) to deduce the missing thermodynamic specifications of this crystal compound.

$NaNbO_3$:Mn features

The influence of Mn dopant ions on the transition between ferroelastic and antiferroelectric phases (called *P* - *R*) in sodium niobate has been studied by Molak [5], and the heat capacity of the antiferroelectric *P* - *R* transition was reported in work by Molak *et al.* [6].

The interest in electrical features of the $NaNbO_3$ doped with the Mn ions was also focused. Such a system would join the high resistance of the niobate materials with the active role of the dopant Mn ions. Electrical measurements were conducted for both the Mn-doped $NaNbO_3$ and the stoichiometric $NaNbO_3$ crystals to discern the role of the doping with these alio-valence ions. In former works, conducted on the pure and the Mn-doped sodium niobate crystals, it has been shown that the transition from the insulator state (where the resistance was higher than ~10 GΩ) to the metallic properties with resistance value of the order of 10-100 Ω, has been induced in the oxygen-deficient samples by reducing in 4% H_2 in Ar gas (~10^{-6} mbar H_2), at 1070 K prior to the electric measurement Molak *et al.* [7]. The transition to the metallic state was induced for both types of composition, in the pure and

the doped ones. However, it has been found that the Mn dopant ions stabilize the metallic type of temperature dependence of the resistance in the range from 1070 K down to room temperature.

Moreover, the spatially non-homogeneous distribution of the electric conductivity was found. The highly conducting filaments, which appeared in the oxygen-deficient sodium niobate, were related to the easy diffusion paths distributed in the crystal lattice. It has been shown that apart from the diffusion of oxygen ions, the Na ions migrate toward the surface of crystal samples exposed to the chemical and electrical gradients (Molak *et al.* [8], Alvarado *et al.* [9]).

The X-ray photoelectron spectroscopy (XPS) study has been conducted on the series of the purposefully modified $NaNbO_3$:*x*Mn crystal samples (Kubacki *et al.* [10], Ksepko *et al.* [11], Pilch *et al.* [12]). It has been reported that doping with Mn ions, which replace Nb ions, influences its valence band. A tail in the density of state emerges at the top of the valence band in the case of the crystal Mn-doped crystals. Such effect has been assigned to the hybridization of the Mn ions with the O 2p and Nb 4d states since Mn ions built into the Nb sublattice of the $NaNbO_3$ crystal lattice (Wolska *et al.* [13], Ławniczak-Jabłońska *et al.* [14], Molak *et al.* [15]).

The measurements were conducted for both the Mn-doped $NaNbO_3$ and the stoichiometric $NaNbO_3$ crystals to discern the role of the doping with this alio-valence Mn ion. The interest was focused on the $NaNbO_3$ doped with the Mn ions. Such a system would join the high resistance of the niobate materials with the active role of the dopant Mn ions, which may influence structural stability and the electrical and optical features. Thermodynamic specifications like partial pressures, equilibrium constant, sublimation enthalpy, heat of formation, Gibb's energy, entropy, and activity of sodium in this crystal compound are known for $NaNbO_3$ from earlier work, but not for Mn-doped $NaNbO_3$.

Experimental

Mass spectrometry measurement

The vaporization studies of the $NaNbO_3$:*x*%Mn were conducted at the Forschungszentum Jülich, by Knudsen effusion mass spectrometry (KEMS) with use of the MAT 271 type instrument supplied by Finnigan MAT of Bremen, Germany. We have substantially

modified it, and it was completely computer controlled. The principal setup of a KEMS scheme was shown in the articles by Kobertz *et al.* [4, 16].

The vapor species, $M(g)$, entering the ion source as a molecular beam were subjected to ionization by electron impact ($M(g) + e^- \rightarrow M(g)^+ + 2\ e^-$) with an emission current, $E_i = 0.5$ mA, and electron energy $E_{e^-} = 70$ eV. A set of collimating lenses focused the ion beam and, on the way to the entrance slit of the mass analyzer, the ion's kinetic energy was boosted by an accelerating potential of 8 kV. We used a resolution of 1200 to supply higher sensitivity, which was good enough to distinguish between all species and their direct mass neighbors under consideration. Our studies were generally done with ion counting of the ionized species to avoid a mass discrimination caused by the multiplier. The ion counts were converted to an intensity signal of a potential drop.

An assembly of an outer tungsten container lined with an inner iridium Knudsen cell is the best for oxide systems. Iridium is oxidation-resistant at temperatures even higher than the range of the studies; Therefore, only the sample controlled the oxygen partial pressure. An effusion orifice with a diameter of 0.3 mm was sufficient for studies on oxide systems without diffusion-controlled vaporization. An automatic pyrometer of the ETSO-U type supplied by Dr Georg Maurer GmbH, Kohlberg, Germany, measures the temperature in a blackbody hole in the Knudsen cell below the sample. All temperature detectors were calibrated *in-situ* using the melting points of silver and gold.

Sixteen measurements on $NaNbO_3$:*x*%Mn were conducted with the KEMS in the temperature range between 1020 and 1500 K. Five automatic runs on pure $Na_2O(c)$ with 8 to 12 different temperatures were performed to determine the vapor phase features and to establish a reference state (Kobertz [16]). The identical procedure, applied to the runs on nominal $NaNbO_3$:*x*%Mn samples, allowed a direct comparison of the mass spectra. The initial temperature of the vaporization measurements was the lowest temperature where the vapor species could be detected sufficiently.

The temperature-dependent vaporization studies were performed in different runs on increasing the temperature stepwise in 10 to 20 K min^{-1}. In this mode, the system releases more gaseous molecules (due to vapor pressure increases) at any subsequent step, and the equilibrium process is driven by a solid-vapor one, which goes faster. The calibration of the Knudsen cell - mass spectrometer system was performed by the vaporization of pure silver. The Mn-doped sodium niobates were studied in the same Ir-Knudsen cell as the $NaNbO_3(c)$ crystal with an effusion orifice (0.3 mm), electron emission (0.5 mA), and electron energy

(70 eV). The amount of sample ranged from 40 to 80 mg. After each measurement, the cell was first cleaned and then baked out in the mass spectrometer unless the ion intensity of Na^+ was below the detection limit in the range of the vaporization studies.

Sample preparation and description

Sodium niobate crystals doped with Mn were obtained from high temperature melted salts Na_2CO_3-Nb_2O_5-B_2O_3 solutions. The Nb_2O_5 (Fluka, purity > 99.9%) and Na_2CO_3 (Reachim, purity > 99.8%) constituents were mixed following the $NaNbO_3$ stoichiometry. MnO (Aldrich, purity > 99%) was added with the aim to produce crystals nominally doped with 0.1 and 1 wt% Mn (Molak *et al.* [17], Molak [5], Kubacki *et al.* [10]) and therefore noted inside this manuscript as 0.1 wt% and 1 wt%.

Suitable flux content was found experimentally. A Pt crucible, filled with the mixture, was placed in a furnace with a temperature gradient ~10 K cm^{-1} to provide convection of the solution constituents. The mixture was melted at 1340 K, held at this temperature for 2 h and then cooled at a rate of 2 K h^{-1} to 1140 K, and then the solvent was poured off.

Transparent cubes and plates with dimensions of several millimeters were obtained. The pure $NaNbO_3$ crystals were transparent. Depending on the Mn concentration, the doped with Mn crystals were yellowish to brown. It should be mentioned that an uncontrolled small amount of impurity ions, originating from initial substrates, may be present even in the nominally pure samples.

The actual content of the Mn dopant was lower than the nominal concentration introduced into the initial mixture. It had been found that there is a solubility limit of Mn ions within the sodium niobate host on ≈ 1 wt% (≈3 mol%) level. It was related to precipitation of the Mn ions observed in $NaNbO_3$:*x*Mn crystals (Molak *et al.* [17], Molak [5], Molak *et al.* [7]). The non-homogeneous distribution of the Mn in the crystals was found with the use of the transmission microscopy test (Molak [5]). It has occurred that the Mn ions replace the Nb ions has been deduced from the EPR spectrum analysis (Molak *et al.* [18]), XPS spectrum analysis (Kubacki *et al.* [10]), and confirmed with the use of the XANES test (Wolska *et al.* [13]).

The room temperature XRD patterns showed the same set of Bragg's lines for both, the $NaNbO_3$ and $NaNbO_3$:Mn samples. Minor differences in intensity of several lines were seen. They were identified and indexed in accordance with orthorhombic symmetry with space

group Pbcm (ICDD catalogue No. 57) and in agreement with literature data (Kruczek *et al.* [19], Sakowski-Cowley *et al.* [20], Molak *et al.* [21]). The determined lattice parameters values were $a = 5.501$Å, $b = 5.666$Å, and $c = 15.520$Å. The main result of this study is related to the experimental evidence that the identical XRD patterns indicated the same global symmetry of both pure and Mn-doped $NaNbO_3$ crystals (Molak [5]). The local chemical concentration was figured out for the $NaNbO_3$ and Mn-doped $NaNbO_3$ lamellae by the EDX method. The concentration of the Mn ion varied depending on the place chosen for the measurement of the $NaNbO_3$:Mn lamella sample, *i.e.,* Mn-rich and Mn-free places were found by Molak *et al.* [5, 17, 21].

Manganese ions, which replace the Nb^{5+} ions in sodium niobate crystal lattice, can exhibit several ionic states: Mn^{2+}, Mn^{3+}, Mn^{4+} or form covalent bonding (Molak *et al.* [15], Wolska *et al.* [13]). In the case of low concentration of the Mn, the charge imbalance was stabilized by the oxygen non-stoichiometry in the neighborhood of Mn ions (Molak [5, 22], Kubacki *et al.* [10]). The demanded higher concentration of Mn in the sodium niobate crystal host was reached by the introduced hetero-valence ions. In this case, Bi and Pb ions for the co-doping have been chosen, that enabled the necessary charge compensation. Moreover, precipitation of Mn or local increase in its concentration with an apparent change in local crystal lattice symmetry was detected Molak *et al.* [7].

The Knudsen mass spectrometer has a detection limit of about 10^{-18} mol, which enables detecting any trace elements given in Table 1. If these elements are not involved in vapor phase reactions, they will not disturb the equilibrium constant. Under Knudsen conditions, all gas species behaved ideal. If the trace elements take part in condensed phase processes, which will change the vaporization behavior, then they would have been found and detected in the mass spectra. From that point of view, the quality of the crystals without unwanted impurities has been remarkably high concerning the vaporization studies.

Table 1: Element analysis of $NaNbO_3$: *x*Mn sample by ICP-OES. The concentration is given in wt%. The standard error is 3% of the analyzed values.

Element	x Mn wt%$^{-1}$		Element	x Mn wt%$^{-1}$	
	0.1	1		0.1	1
Na	13.9	13.9	Ni	<0.05	<0.05
Nb	56.4	56.5	Sr	<0.02	<0.02
O	28.6 ± 1	28.7 ± 0.3	Ti	<0.6	< 0.6
Mn	<0.01	<0.01	Zn	<1.14	<1.14

Transferring the weight% to mol% exhibited the perfect perovskite ratio of Na:Nb:O = 1:1:3 (ABO_3). Moreover, the obtained Mn content of 1.8 10^{-4} mol indicated that Mn-doped $NaNbO_3$ material was provided.

Results

Vaporization studies

Nine measurements on nominal $NaNbO_3$:0.1%Mn and seven measurements on nominal $NaNbO_3$:1%Mn have been conducted with the Knudsen effusion mass spectrometer in the temperature range between 1020 and 1500 K.

Only Na^+ and O_2^+ but no Na_2O^+ ions were detected, and they originated from the species Na(g) and O_2(g) over $NaNbO_3$(c) as well as over $NaNbO_3$:*x*Mn(c). Following Eqs. (1) and (12), the reactions show incongruent vaporization (*x* was either 0.1 or 1 wt%), just like reactions (2), (5), (6), and (7). The reactions having Nb_2O_5(c) as a vaporization product were not considered. It was needed to show the vaporization and the equilibrium equations of Na_2O(c) as a reference for a comparison with the niobium oxide-containing compounds. The experimental data were given by Kobertz [16] and brought here into the following figures (Figs. 1 and 2). NbO_2(c) showed no measurable gas species in the temperature range of the study. For the partial pressure of O_2, it was assumed that the vaporization process is congruent with respect to oxygen.

Reactions for Na_2O(c) are as follows:

$$Na_2O(c) \Leftrightarrow Na_2O(g) \quad (1)$$

$$Na_2O(c) \Leftrightarrow 2\,Na(g) + 0.5\,O_2(g) \quad (2)$$

$$K_p(1) = \frac{pNa_2O(g)}{p^0}\,\frac{1}{aNa_2O(c)} \quad (3)$$

$$K_p(2) = \left(\frac{pNa(g)}{p^0}\right)^2 \sqrt{\frac{pO_2(g)}{p^0}} \frac{1}{aNa_2O(c)} \quad (4)$$

In the equations (13) and (4), $p^\circ = 1$ atm, and the activity, a of aNa2O(c) is equal to 1. The standard pressure p° in atmosphere was used to follow an easy way making the equilibrium constant Kp dimensionless to take the logarithm of its value.

Because of the fact of nonexistent Na2O(g) in the vapor reaction (1) as well as $K_p(2)$ (eq. (3)) was disregarded in the Mn-doped sodium niobate studies. Ions of niobium and manganese-containing gas species were also not detected in this temperature range, in which the samples were studied. Hence, Mn must be bounded in the perovskite structure as manganese oxide.

As an orientation the pressures in Pa of the pure compounds at 1200 K taken from database IVTANTHERMO [23] are for Na2O(g) 1.9 10^{-3}, Mn(g) 5.1 10^{-1}, MnO(g) 9.2 10^{-11}, MnO2(g) 1.2 10^{-8}, and NbO2(g) 5.1 10^{-11}. The pressure over Na2O(c) is extensively studied in the work of Kobertz [16] (Table 2).

MnO is as stable as NbO2(g) and could also not be detected in the vapor phase. In contrast to this, metallic Mn(g) has a partial pressure, which would be high enough in the temperature range under consideration to find such ions in the vapor phase. For completeness, the main possible vaporization reactions and associated equilibrium constants are listed below, but for the evaluation, only reactions (2), (6), and (12) were in the consideration. Eq. (5) is multiplied by 2 of Eq. (6) to compare Eq. (2) directly regarding the molarity of the dominant Na(g) for the activity determination (Eq. (21)).

Reactions for NaNbO3(c):

$$2\ NaNbO_3(c) \Leftrightarrow 2\ Na(g) + O_2(g) + 2\ NbO_2(c) \quad (5)$$

$$NaNbO_3(c) \Leftrightarrow Na(g) + 0.5\ O_2(g) + NbO_2(c) \quad (6)$$

$$2\ NaNbO_3(c) \Leftrightarrow 2\ Na(g) + 0.5\ O_2(g) + Nb_2O_5(c) \quad (7)$$

$$K_p(5) = \left(\frac{pNa(g)}{p^0}\right)^2 \frac{pO_2(g)}{p^0} \frac{(aNbO_2(c))^2}{(aNaNbO_3(c))^2} \quad (8)$$

$$K_p(6) = \frac{pNa(g)}{p^0} \sqrt{\frac{pO_2(g)}{p^0}} \frac{aNbO_2(c)}{aNaNbO_3(c)} \quad (9)$$

$$K_p(7) = \left(\frac{pNa(g)}{p^0}\right)^2 \sqrt{\frac{pO_2(g)}{p^0}} \frac{aNb_2O_5(c)}{(aNaNbO_3(c))^2} \quad (10)$$

In the equations (13), (9), and (10), $p^\circ = 1$ atm and the activity a of $a\mathrm{NbO_2(c)}$, $a\mathrm{Nb_2O_5(c)}$, and $a\mathrm{NaNbO_3(c)}$ is equal to 1.

Reactions for $\mathrm{NaNbO_3}$:xMn(c):

$$2\ \mathrm{NaNbO_3}{:}x\mathrm{Mn(c)} \Leftrightarrow 2\ \mathrm{Na(g)} + \mathrm{O_2(g)} + 2\ (\mathrm{NbO_2}{:}x\mathrm{Mn(c)}) \quad (11)$$

$$\mathrm{NaNbO_3}{:}x\mathrm{Mn(c)} \Leftrightarrow \mathrm{Na(g)} + 0.5\ \mathrm{O_2(g)} + \mathrm{NbO_2}{:}x\mathrm{Mn(c)} \quad (12)$$

The equilibrium constants for the above-given vaporization reactions are the same as for un-doped sodium niobate:

$$K_\mathrm{p}(11) = \left(\frac{p\mathrm{Na(g)}}{p^0}\right)^2 \frac{p\mathrm{O_2(g)}}{p^0} \frac{(a\mathrm{NbO_2}{:}\mathrm{xMn(c)})^2}{(a\mathrm{NaNbO_3}{:}\mathrm{xMn(c)})^2} \quad (13)$$

$$K_\mathrm{p}(12) = \frac{p\mathrm{Na(g)}}{p^0} \sqrt{\frac{p\mathrm{O_2(g)}}{p^0}} \frac{a(\mathrm{NbO_2}{:}\mathrm{xMn(c)})}{a(\mathrm{NaNbO_3}{:}\mathrm{xMn(c)})} \quad (14)$$

In the equations (13) and (14), $p^\circ = 1$ atm and the activity a of $a\mathrm{NbO_2}$:xMn(c) and $a\mathrm{NaNbO_3}$:xMn(c) is equal to 1.

Partial pressures

Partial pressures $p(\mathrm{i})_T$ of species Na and $\mathrm{O_2}$ at the temperature T over the samples were obtained in Pa from the equation **Fehler! Verweisquelle konnte nicht gefunden werden.**.

$$p(i)_T = \mathrm{k}\ \frac{\sum I(i)T}{\eta(i)\,\gamma(i)\,\sigma(i)} \quad (15)$$

where k is the pressure calibration factor and $\Sigma I(i)$ is the sum of the intensities of the ions originating from the same neutral precursor i. In the case of silver (applied as a reference), it is only the intensity of the stable isotope ^{107}Ag. The correction to 100% intensity was done by the isotopic abundance factor. $\eta(i)$ is the isotopic abundance factor and $\sigma(i)$ stands for the ionization cross-section of the species (i). $\gamma(i)$ is the multiplier factor of ion (i) that describes a mass- and molecule structure-dependent value of secondary electron emission from the first dynode of a multiplier. The value $\gamma(i) = 1$, since an ion counting system was used here in the KEMS. The ionization cross-sections used in pressure determination for the gaseous species, which were $\sigma(\mathrm{Na}) = 2.77$, $\sigma(\mathrm{O_2}) = 2.5$, and $\sigma(\mathrm{Na_2O}) = 7.056$, were mean values reported by Mann [24] and Deutsch *et al.* [25, 26]. The pressure calibration factor k was determined using silver vaporization studies in the temperature range from 990 to 1200 K, using the same Knudsen cell as in the studies conducted for the oxide samples. To avoid an alloying of Ag with Ir, an $\mathrm{Al_2O_3}$ inline crucible was used. More details were provided by Kobertz [16].

From the partial pressures, as seen in **Fehler! Verweisquelle konnte nicht gefunden werden.**, evaluated with the ion intensities at the chosen temperature range using Eqs. (15), (6), and **Fehler! Verweisquelle konnte nicht gefunden werden.**), the corresponding equilibrium constants following Eqs. (), (9) and (2) were figured out.

The ratio $[n(\mathrm{Na})/n(\mathrm{O_2})]$ in the effusate was taken to be *2* in Eqs. (6), (12) or *4* in Eq. (2). By employing the Knudsen effusion equation, $p(i) \sim \sqrt{\frac{1}{M(i)}}$, this assumption translates to $[p(\mathrm{Na})/p(\mathrm{O_2})]$ inside the Knudsen cell are either $= 2$ or 4 $[M(\mathrm{Na})/M(\mathrm{O_2})]^{0.5}$. Concerning these relations, the partial pressure of O_2 over Na_2O(c) follows the relation Eq. (16a, 16b), either for ratio 2:

$$p(\mathrm{O_2}) = \frac{1}{2}\sqrt{\frac{M(\mathrm{O_2})}{M(\mathrm{Na})}}\, p(\mathrm{Na}) = 0.590\, p(\mathrm{Na}) \qquad (16a)$$

or for ratio 4:

$$p(\mathrm{O_2}) = \frac{1}{4}\sqrt{\frac{M(\mathrm{O_2})}{M(\mathrm{Na})}}\, p(\mathrm{Na}) = 0.295\, p(\mathrm{Na}) \qquad (16b)$$

The equilibrium constant for the reactions in Eqs. (2), (6), and **Fehler! Verweisquelle konnte nicht gefunden werden.**), was reorganized by replacing the partial pressure for O_2, $p(O_2)$ with Eqs. (16a, 16b) to get an oxygen-independent relation for $K_p(2) = 0.295\sqrt{\left[\frac{p(Na)}{p^0}\right]^3}$ and for $K_p(6 \text{ and } 12) = 0.590\sqrt{\left[\frac{p(Na)}{p^0}\right]^3}$.

The partial pressures in Pa and the Arrhenius functions of Na(g) over Na_2O(c), $NaNbO_3$(c) and, common functions over both, nominal $NaNbO_3$:0.1wt%Mn(c) together with nominal $NaNbO_3$:1wt%Mn(c) are shown in Figure 1. The partial pressure of O_2(g) is omitted in the figure for a well-arranged graph, but their functions are posted in Table 2.

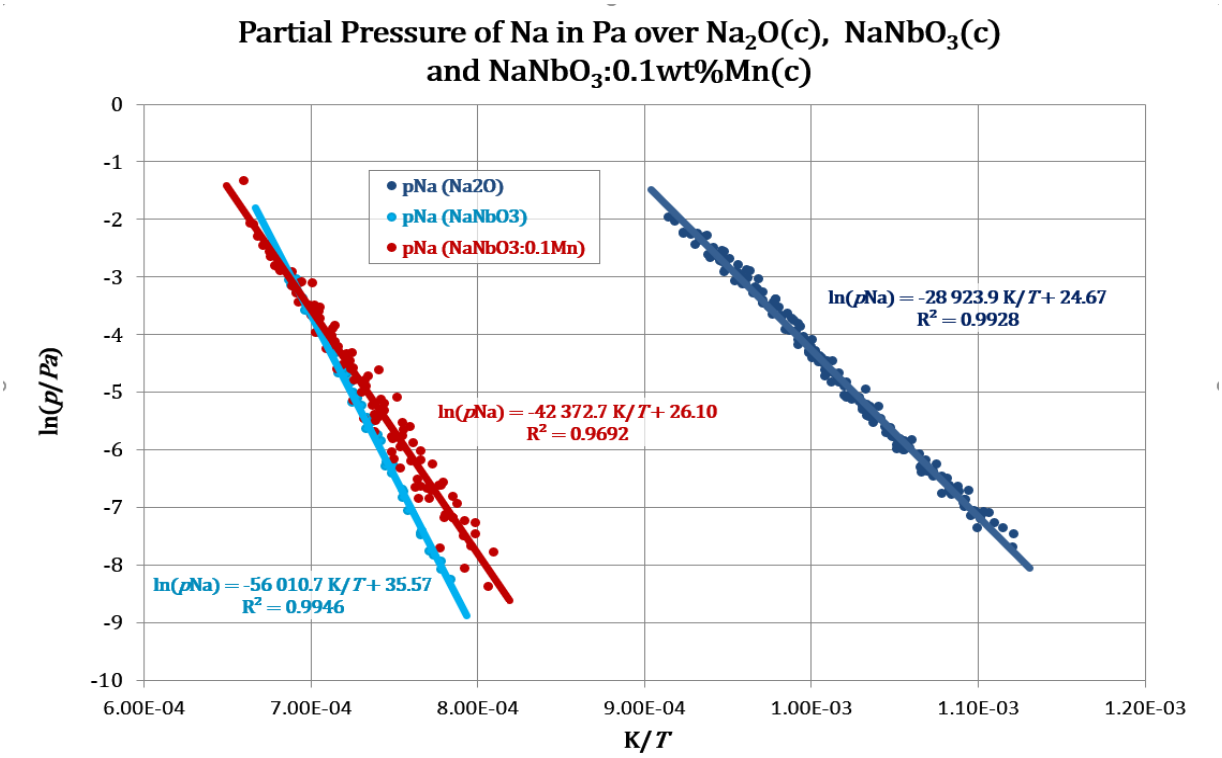

Fig. 1: Partial pressures in Pa of Na(g) and their functions over Na_2O(c) (Eq. (2)), $NaNbO_3$(c) (Eq. (6)), and nominal $NaNbO_3$:0.1wt%Mn(c) (Eq. (12))

There was almost no difference about the functions of the equilibrium constants for the reactions with the nominal 0.1 wt% and 1 wt% Mn-doped sodium niobates, as diagramed in Figure 2. However, this effect would be expected from the analysis of data given in Table 1. Probably the tested samples under consideration had the same actual Mn concentration although they were taken from a different nominal synthesis of bulk with 0.1 and 1 wt% Mn content but with a real concentration between 0.01 wt% and 0.3 wt% (Kubacki *et al.* [9], Molak *et al.* [17]).

Contrary, the method of KEMS is to be up to distinguish even small and relevant changes in element concentration and distribution in a sample.

Such deduction is justified if a small amount of sample is taken from a large bulk with inhomogeneous distribution of doping ions clusters in the crystal.

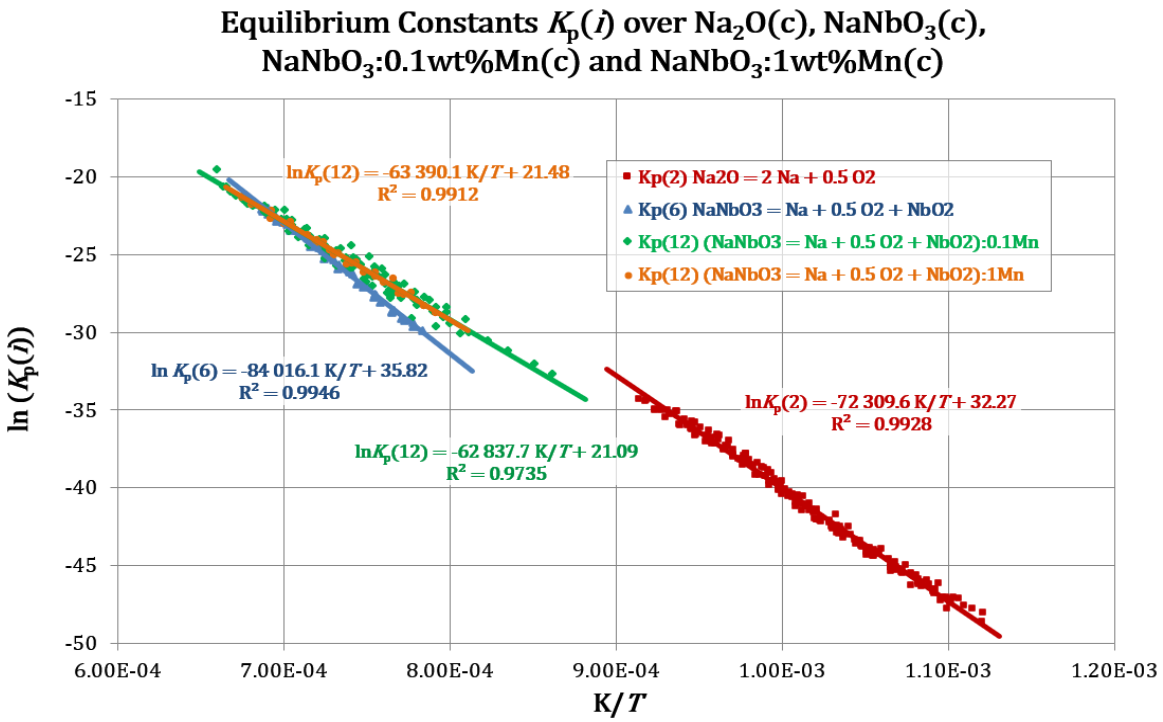

Fig. 2: Natural logarithm of the equilibrium constants Kp(i) numbering (i = (2), () and (12)) of the Eqs (4), (9), and (14) as a function of the inverse absolute–temperature, 1/T, of vapor species obtained in the last 3 runs of a measurement series. Kp is based on pressures in atmosphere.

Gibb's energy ($\Delta_r G_T^0$)

From the pressure equilibrium constants K_p(11) and K_p(12), described by Eqs. (13) and (14), the standard Gibb's energy functions for the reactions about Na(g) are described by Eqs. () and (18) for nominal $NaNbO_3$:0.1%Mn(c). and by Eqs. () and (20) for nominal $NaNbO_3$: 1%Mn(c). Functions valid for the temperature range from 1250 to 1450 K were found to be for $NaNbO_3$:0.1%Mn(c):

$$\Delta_r G_T^0 = -\mathrm{R}\,T\,ln\mathrm{K}_p^0(11) = -(3.54 \pm 0.08)\ 10^{-1}\ T + (1049.3 \pm 14)\ \mathrm{kJ\ mol^{-1}} \quad (17)$$

$$\Delta_r G_T^0 = -\mathrm{R}\,T\,ln\mathrm{K}_p^0(12) = -(1.77 \pm 0.02)\ 10^{-1}\ T + (524.6 \pm 5)\ \mathrm{kJ\ mol^{-1}} \quad (18)$$

and for $NaNbO_3$: 1%Mn(c):

$$\Delta_r G_T^0 = -\mathrm{R}\,T\,ln\mathrm{K}_p^0(11) = -(3.58 \pm 0.08)\ 10^{-1}\ T + (1054.8 \pm 14)\ \mathrm{kJ\ mol^{-1}} \quad (19)$$

$$\Delta_r G_T^0 = -\mathrm{R}\,T\,ln\mathrm{K}_p^0(12) = -(1.79 \pm 0.02)\ 10^{-1}\ T + (527.4 \pm 5)\ \mathrm{kJ\ mol^{-1}} \quad (20)$$

Gibb's energy, regarding the vaporization reaction of sodium in the Mn-doped sodium niobates, has been deduced each with the last 3 runs of a measurement series (Figure 3).

One can realize that there is nearly no difference in the results between nominal $NaNbO_3$:0.1%Mn and nominal $NaNbO_3$:1%Mn.

It has to be mentioned that the desired nominal Mn-concentrations are not the actual concentrations, but inside of the solubility range (Rezhnichenko et al. [27] Molak *et al.* [7]], [Molak *et al.* [21]).

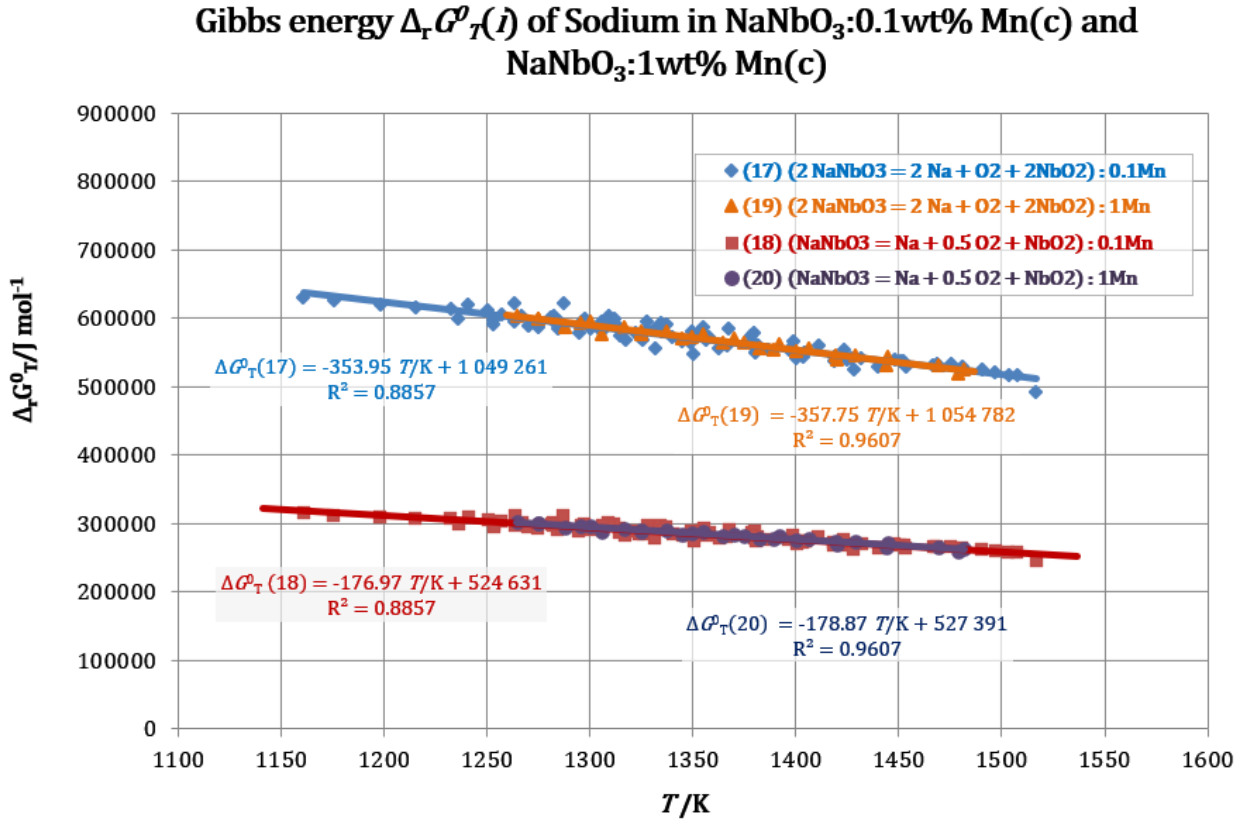

Fig. 3: Gibb's energy of sodium over nominal $NaNbO_3$:0.1wt%Mn(c) and nominal $NaNbO_3$:1wt%Mn (c) between 900 and 1450 K calculated from $K_p(11)$ and $K_p(12)$ given in Eqs. (13) and (14). The Gibb's energy $\Delta_r G_T^0$ (17) and $\Delta_r G_T^0$ (19) represent 2 Mol of each Mn doped sodium niobate regarding the molarity of the dominant Na(g). *K*p is based on pressures in atmosphere.

Table 2 provides a summary of the results of the vaporization studies conducted on sodium niobate and Mn-doped sodium niobate crystals, including the equilibrium constants (K_p), the partial pressures of Na(g) and O_2(g), and Gibb's energies of equilibrium reactions with gaseous sodium. The unmarked data (white background) were taken from Kobertz [16], and Kobertz *et al.* [4] papers.

Table 2: Summary of data for: equilibrium constants K_p, partial pressure p of Na(g), O_2(g), over Na_2O(c), $NaNbO_3$(c) $NaNbO_3$:xMn(c) with nominal $x = 0.1$ wt% and 1 wt% Mn, and Gibb's energy, $\Delta_r G_T^0 = -\Delta_r S_T^0\ T + \Delta_r H_T^0$, ($\Delta S$ in kJ mol^{-1} K^{-1} and ΔH in kJ mol^{-1}). Unmarked data (white background) are from [16], [4].

Equilibrium constant based on pressures in atmosphere	Temperature range /K	$\ln K_p = A\frac{K}{T} + B$	
		A	B
K_p(2) (Na_2O=2 Na + 0.5 O_2)	900 - 1165	-72309.6	32.27
K_p(6) ($NaNbO_3$=Na + 0.5 O_2+NbO_2)	1250 - 1465	-84016.1	35.82
K_p(12) ($NaNbO_3$=Na + 0.5 O_2+NbO_2):0.1%Mn	1150 - 1490	-62837.7	21.09
K_p(12) ($NaNbO_3$=Na + 0.5 O_2+NbO_2): 1%Mn	1260 - 1490	-63390.1	21.48
Gibb's energy based on pressures in atmosphere	Temperature range /K	$\Delta G_r = A\frac{T}{K} + B =$ -R $T\ln(K_p)$	
		$A = (\Delta_r S_T^0)$	$B = (\Delta_r H_T^0)$
K_p(5) (2 $NaNbO_3$=2 Na + O_2+NbO_2)	1250 - 1465	-(5.87 ± 0.08) 10^{-1}	1386.2 ± 14
K_p(6) ($NaNbO_3$=Na + 0.5 O_2+NbO_2)		-(2.94 ± 0.02) 10^{-1}	693.1 ± 5
K_p(11) (2 $NaNbO_3$=2 Na + O_2+NbO_2):0.1%Mn	1150 - 1490	-(3.54 ± 0.08) 10^{-1}	1049.3 ± 14
K_p(12) ($NaNbO_3$=Na + 0.5 O_2+NbO_2):0.1%Mn		-(1.77 ± 0.03) 10^{-1}	524.6 ± 5
K_p(11) (2 $NaNbO_3$=2 Na + O_2+NbO_2): 1%Mn	1260 - 1490	-(3.58 ± 0.08) 10^{-1}	1054.7 ± 14
K_p(12) ($NaNbO_3$=Na + 0.5 O_2+NbO_2): 1%Mn		-(1.79 ± 0.03) 10^{-1}	527.4 ± 5

Partial pressure in Pa		Temperature range /K	$\ln(p/\text{Pa}) = A\frac{K}{T} + B$		
Molecule	(source)		A	B	p(i)$_{1200K}$ /Pa
Na	(Na_2O)	900 - 1165	-28923.9	24.67	1.76 10^{0}
O_2	(Na_2O)		-28923.9	23.45	5.18 10^{-1}
Na	($NaNbO_3$)	1250 - 1465	-56010.7	35.57	1.50 10^{-5}
O_2	($NaNbO_3$)		-56010.7	34.35	4.44 10^{-6}
Na	($NaNbO_3$:0.1%Mn)	1150 - 1490	-41891.8	25.75	1.05 10^{-4}
O_2	($NaNbO_3$:0.1%Mn)		-41891.8	25.22	6.19 10^{-5}
Na	($NaNbO_3$:1%Mn)	1260 - 1490	-42260.1	26.01	1.00 10^{-4}
O_2	($NaNbO_3$:1%Mn)		-42260.1	25.48	5.91 10^{-5}

The mass spectra data of Na_2O, $NaNbO_3$, and $NaNbO_3$:xMn do not have a common temperature range for the studies under consideration. Since the determination coefficient (R^2-value) of the linear regression is close to one, an extrapolation of the linear function for $NaNbO_3$, and $NaNbO_3$:xMn of 100 K to lower, and for Na_2O of 100 K to higher temperature could be allowed. The extrapolated common range (1100 – 1250 K) allowed the determination the thermodynamic activities of sodium oxide (Na_2O) in sodium niobate by using equation (6).

The evaluation of the thermodynamic activity for Na_2O using the equilibrium constants $K_p(2)$ (Eq. ()) and $K_p(12)$, (Eq. ()) or, alternatively, using the measured ion intensity ratios as shown in Eq. (21) with x=0.1 and 1 wt% Mn.

$$a_{(T)}(Na_2O) = \frac{K_p(12)}{K_p(2)} = \frac{p^0\, pNa^{NaNbO_3:xMn}_{(T)} \sqrt{pO_{2\,(T)}^{NaNbO_3:xMn}}}{(pNa)^2\,{}^{Na_2O}_{(T)} \sqrt{pO_{2\,(T)}^{Na_2O}}} = \frac{\left[I(Na^+)\sqrt{I(O_2^+)}\right]^{NaNbO_3:xMn}_{(T)}}{\left[I^2(Na^+)\sqrt{I(O_2^+)}\right]^{Na_2O}_{(T)}} \qquad (6)$$

The thermodynamic activities of Na_2O as figured out with Eq. (21) at 1200 K are $3.74 \cdot 10^{-2}$ for nominal $NaNbO_3$:0.1Mn and $3.48 \cdot 10^{-2}$ for nominal $NaNbO_3$:1%Mn. In comparison to these values, the activity for $NaNbO_3$ taken from Kobertz *et al.* [4] is $2.02 \cdot 10^{-3}$, pointing out an about eighteen times higher stability of undoped sodium niobate.

Discussion

The doped samples were not perfect in terms of the desired Mn-concentration. It was found that both prepared samples exhibited a Mn concentration that was 10 times respectively 100 times lower than initially wanted (Table 1). For a description of the raw material, a small part of the bulk was analyzed, and the result confirmed the perovskite structure of the samples under consideration. This probe was used up and another part of the bulk was taken for the studies. Kubacki *et al.* [10]], Molak *et al.* [17], Molak *et al.* [21] have estimated a solubility limit of Mn ions within the sodium niobate of about ≈ 1 wt% (≈3 mol%). Even with the inhomogeneous concentration in the bulk the subsamples used in the studies were single crystals without any second phase. The activity of Na_2O follows Raoult's law depending on the Mn-concentration if it is inside the solubility range. The analyzed Mn amount in the samples under consideration formed a solid solution with sodium niobate.

Since the covalent radius of Mn (139 pm) is smaller than those of Na (166 pm) and Nb (164 pm) (pm = 10^{-12} m), Mn can replace either Na or Nb in the crystal lattice.

X-ray photoelectron spectroscopy experiments conducted by Kubacki *et al.* [10] have indicated that Mn ions replace Nb^{5+} ions, and Sakowski *et al.* [20] have described that the symmetry of $NaNbO_3$:*x*Mn single crystals remains unchanged if the actual concentration of Mn dopant is lower than 1 wt%.

In contrast to this, Bykov *et al.* [28] proposed, based on EPR spectrum analysis, that Mn^{2+} ions replace Na^+ ions.

The partial pressure of Na(g) and O_2(g) is higher over Mn-doped $NaNbO_3$ than over the $NaNbO_3$ single crystal (Figure 1). This is only possible if the thermodynamic activity of sodium is higher (sample is less stable) in the doped sample than in the pure one. Indeed, it was found that the activity of the Mn-doped samples at 1200 K is about 20 times higher. The estimated values are $3.2 \cdot 10^{-2}$ for nominal $NaNbO_3$:0.1%Mn, $3.0 \cdot 10^{-2}$ for nominal $NaNbO_3$:1%Mn, and $1.8 \cdot 10^{-3}$ for the pure $NaNbO_3$ ([16])

The most stable un-doped structure according to the activity of sodium is $NaNbO_3$. Consequently, this means that manganese seems to weaken the bonding, either by replacing niobium or by moving into interstitial places of the structure.

This is also indicated by a lower sublimation enthalpy of the Mn-doped sample in comparison with the un-doped one (Table 3). The unmarked data (white background) were taken from Kobertz [16], and Kobertz *et al.* [4] papers. In respect to the clarity of Fig. 1, the partial pressures of Na(g) and O_2(g) over nominal $NaNbO_3$:1%Mn are not shown since they are nearly the same as for nominal 0.1% Mn. However, the small differences between 0.1% Mn- and 1% Mn-doped samples can be seen in Figure 2, where the equilibrium constants of $K_p(2)$ of Na_2O(c), $K_p()$ of $NaNbO_3$(c) and $K_p(12)$ of nominal $NaNbO_3$:0.1%Mn(c) and nominal $NaNbO_3$:1%Mn(c) are depicted. The small differences also go confirm in accordance with the small differences in the element analysis of Mn (Table 1). The minor differences between 0.1% and 1% Mn affirming a conclusion of a small difference between the sample compositions under consideration and contrary to the nominal set-up. Nevertheless, in summary the effect on doping $NaNbO_3$ with Mn is clearly identified.

Replacing sodium with manganese would reduce the activity (Raoult's law [29]), and the vapor pressure would be below that of pure sodium niobate, which has not been observed in the measurements. This implicates that Mn does not replace Na in the perovskite structure.

Table 3: Synopsis of thermodynamic enthalpy data from vaporization studies on Na_2O(c), $NaNbO_3$(c) and $NaNbO_3$with 0.1wt% and 1wt% Mn(c). Unmarked data (white background) are from [16], [4].

Enthalpy of formation $\Delta_f H_T$		0.5 Na_2O(c) + 0.5 Nb_2O_5(c) +0.1Mn = $NaNbO_3$:0.1Mn(c)	$\Delta_f H_{(298)}$ $NaNbO_3$:0.1%Mn	-1242.3 ± 7 kJ mol^{-1}
Enthalpy of reaction $\Delta_r H_T$		Na(g) + 0.5O_2(g) + NbO_2(c) +0.1Mn = $NaNbO_3$:0.1Mn(c)	$\Delta_r H_{(298)}$ $NaNbO_3$:0.1%Mn	-74.9 ± 7 kJ mol^{-1}
Enthalpy of sublimation $\Delta_{sub} H_T$			$\Delta_{sub} H_T$ 2nd law	$\Delta_{sub} H_T$ 3rd law
$NaNbO_3$	1370 K	$Na_{(NaNbO3)}$(c) = Na(g)	464.7 ± 9 kJ mol^{-1}	439.4 ± 5 kJ mol^{-1}
Na_2O	1000 K	$Na_{(Na2O)}$(c) = Na(g)	242.6 ± 3 kJ mol^{-1}	240.7 ± 1 kJ mol^{-1}
$NaNbO_3$:0.1%Mn	1350 K	$Na_{(NaNbO3:01\%Mn)}$(c) = Na(g)	349.3 ± 2 kJ mol^{-1}	349.8 ± 5 kJ mol^{-1}
$NaNbO_3$:1%Mn	1350 K	$Na_{(NaNbO3:1\%Mn)}$(c) = Na(g)	347.0 ± 7 kJ mol^{-1}	349.5 ± 2 kJ mol^{-1}

Source		Selected reactions	$\Delta_r H_T$ 2nd law	$\Delta_r H_T$ 3rd law	$\Delta_r G_T$	$\Delta_r S_T$
			kJ mol^{-1}			J mol^{-1} K^{-1}
$NaNbO_3$ 1370 K	K_p(5)	2 $NaNbO_3$(c) = 2 Na(g) + O_2(g) + 2 NbO_2(c)	1388.2 ± 2	1386.1 ± 3	580.6 ±9	587.9 ± 6
	K_p(6)	$NaNbO_3$(c) = Na(g) + 0.5O_2(g) + NbO_2(c)	694.6 ± 7	693.6 ±13	290.3 ±9	294.0 ± 5
Na_2O 1000 K	K_p(2)	Na_2O(c) = 2 Na(g) + 0.5O_2(g)	604.6 ± 6	601.7 ± 3	332.8 ± 9	268.9 ± 9
$NaNbO_3$ 0.1 wt% Mn 1350 K	K_p(11)	2 $NaNbO_3$:0.1%Mn(c) = 2 Na(g) + O_2(g) + 2 NbO_2:0.1%Mn(c)	1047.1 ± 3	1049.5 ±13	571.7 ±13	354.0 ± 6
	K_p(12)	$NaNbO_3$:0.1%Mn (c) = Na(g) + 0.5O_2(g) + NbO_2:0.1%Mn (c)	522.4 ± 2	524.8 ±13	285.9 ±14	177.0 ± 5
$NaNbO_3$ 1 wt% Mn 1350 K	K_p(11)	2 $NaNbO_3$:1%Mn (c) = 2 Na(g) + 0.5 O_2(g) + Nb_2O_5:1%Mn(c)	1065.7 ± 6	1048.6 ± 8	565.6 ±10	357.8 ± 7
	K_p(12)	$NaNbO_3$:1%Mn (c) = Na(g) + 0.25O_2(g) + 0.5Nb_2O_5:1%Mn(c)	527.0 ± 7	524.3 ±12	282.8 ±11	178.9 ± 6

Conclusion

The vaporization studies have shown higher partial pressures of Na(g) and O_2(g) over Mn-doped sodium niobates in comparison with pure sodium niobate. A possible explanation for this is that Mn diminishes the bonding site between the oxygen atoms, when the B-site cation Nb is replaced by the smaller atom Mn. The face-centered oxygen atoms, attracted by the smaller atom Mn placed in the oxygen octahedron center, will then lose some bond strength with the result, that sodium is more volatile.

Further, the element sodium is not replaced by the element manganese, otherwise the activity would be smaller, which is not the case. The thermodynamic activity at 1200 K is

$3.7 \cdot 10^{-2}$ for nominal $NaNbO_3$:0.1%Mn, $3.5 \cdot 10^{-2}$ for nominal $NaNbO_3$:1%Mn, and $2.0 \cdot 10^{-3}$ for the pure undoped $NaNbO_3$ showing an about eighteen times the higher stability.

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