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Volatilization of Na₂O and Its Impact on the Processing of Solid Electrolytes

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ABSTRACT

This study explores the volatilization of Na₂O from selected solid and liquid materials, especially from a Na⁺ superionic conductor (NaSICON) with the composition Na_{3.4}Zr₂Si_{2.4}P_{0.6}O₁₂, with the aim of addressing the often arbitrarily chosen amount of additional sodium source used to compensate for mass loss during sintering. The measured and calculated mass losses allow for a more precise estimate of the necessary Na₂O additions during component manufacturing on a larger scale. The practical relevance of this is discussed in the context of manufacturing tape-cast separators for battery applications. In addition, the volatilization of Na₂O from molten sodium silicophosphate glass and sodium phosphate is investigated in different crucible materials and atmospheres to elucidate the impact of experimental parameters, different physical states, and volatilization kinetics. With knowledge of thermodynamic processes and the vapor pressure curve, mass losses can be calculated in very good agreement with the observed data.

1 | Introduction

The volatilization of Na₂O from solids at high temperatures has been well established for more than 100 years, and the first systematic study of the volatility of Na₂O from sodium silicate glasses was carried out in 1932 [1, 2]. Since then, knowledge of the volatilization rates of alkali monoxides and other compounds has become very important in glass production [3, 4, and references therein] and slag formation during the processing of iron-rich ores [e.g., 5, 6]. Aside from these two industrial areas, the volatility of oxides or halides has been used during flux growth of crystals [7, 8]. Crystals of solid electrolytes have also been prepared in this way, such as Li₇La₃Zr₂O₁₂ [9] and NaSICON-type materials Na₃Zr₂Si₂PO₁₂, Na₃Sc₂PO₁₂ [10], and Li_{1+x}Al_xTi_{2-x}(PO₄)₃ [11], as well as Na-β"-alumina [12] and Na-β-alumina [13].

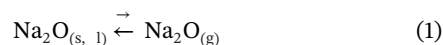
Due to the increased interest in solid-state batteries (this general term here refers to all-solid-state, almost-solid-state, or quasi-solid-state batteries) and the discovery of garnet Li⁺ ionic conductors [14], numerous publications have appeared in the last 15–20 years that recommend the use of a certain excess of Li₂O, that is, sacrificed during sintering at high temperatures in order to obtain the correct stoichiometry of the ionic conductor. This procedure applies not only to garnet-type ionic conductors but also to all oxidic Li⁺ ionic conductors as well as to Na⁺ ionic conductors and their corresponding excess of Na₂O. However, to the best of our knowledge, there are no publications in which the necessary excess of Li₂O or Na₂O was determined by thermogravimetric investigation. While there are several publications in which the excess of alkali monoxide was varied to obtain a correlation with the physical properties [15, 16], the amount of remaining free

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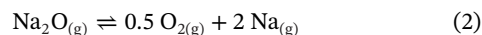
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or excessively vaporized Li_2O or Na_2O remained undefined, and thus the actual composition of the samples remained unknown.

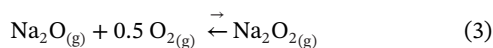
Moreover, there are many reports emphasizing the importance of the sintering setup, including the atmosphere, powder bed, and whether it is unprotected, covered, encapsulated, or covered with a crucible. These reports also note in very general terms that the atmosphere has an impact on the sample surface. The equilibrium between the solid or liquid surface and the gaseous species can be written for the sodium chemistry [17, 18] as:



and



However, Reaction (2) only tends toward the right-hand side when the oxygen partial pressure is very low (e.g., $\approx 3 \times 10^{-18}$ Pa at 900°C [19]). Instead, it is more likely that Na_2O reacts with oxygen to form a mixture of Na_2O and Na_2O_2 [19, 20] according to:



with

$$K = \frac{p(\text{Na}_2\text{O}_2)}{p(\text{Na}_2\text{O}) \sqrt{p(\text{O}_2)}} \quad (4)$$

This means that with decreasing $p(\text{O}_2)$, more $p(\text{Na}_2\text{O})$ is formed to maintain the equilibrium. In other words, more Na_2O evaporates from the sample surface. Measurements performed in argon and air confirm this tendency, as will be discussed later, but the differences are rather small.

Apart from the atmosphere, several other factors have an impact on Na_2O volatilization, including temperature, exposure time, crucible material, composition, and the aggregate state of the material. Some of these parameters are addressed in this work. For this investigation, three materials were selected as model systems: (1) $\text{Na}_{3.4}\text{Zr}_{1.2}\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ as a solid electrolyte, for which the measurements will be of considerable relevance for membrane fabrication; (2) a glass with the composition $\text{Na}_4\text{Si}_4\text{P}_2\text{O}_{15}$; and (3) Na_3PO_4 as a crystalline material with a high melting point. In addition to this orthophosphate, the corresponding metaphosphate NaPO_3 and pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7$ are also included in the measurements with a constant heating rate to elucidate the fundamental differences between these phosphates. However, a more extensive comparative investigation of these materials must be presented elsewhere.

Since all materials are silicophosphates or phosphates, the volatilization of P_2O_5 should also be addressed here. To the best of our knowledge, only a small number of reports have dealt with thermogravimetric investigations of phosphates. Flemish and Tressler reported on the evaporation from SiP_2O_7 and used the mass-loss rate as a function of the carrier gas flow rate to determine an activation energy of 306 kJ/mol in the temperature range of 925°C – 1025°C [21]. Boigelot et al. subsequently measured the mass loss from 70.3 SiO_2 –29.7 P_2O_5 and 87.6 SiO_2 –12.4 P_2O_5

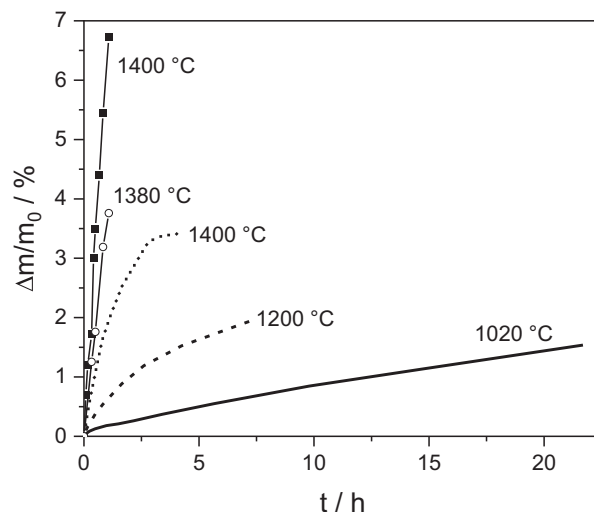
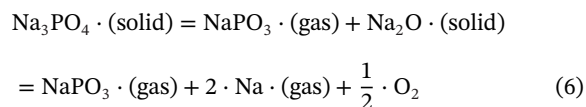
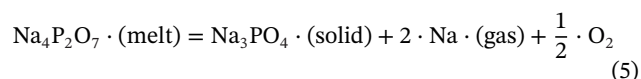


FIGURE 1 | Mass loss of the glasses $\text{LaP}_5\text{O}_{14}$ at 1380°C (open circles), $\text{La}_{0.12}\text{Zn}_{0.33}\text{P}_3\text{O}_8$ at 1400°C (filled squares), and $\text{La}_{0.47}\text{Al}_{0.27}\text{Zn}_{0.52}\text{P}_3\text{O}_{9.13}$ at 1020°C , 1200°C , and 1400°C (straight, dashed, and dotted lines, respectively). Data taken from [24] and [25].

glasses (values in mol%) in an experiment with a constant heating rate up to 1300°C , resulting in 2.9% and 0.7%, respectively. The maximum mass loss occurred between 1100°C and 1175°C [22]. Huang et al. studied the weight changes of SnP_2O_7 , and thermogravimetric analysis showed a decreasing weight from 550°C to 930°C , corresponding to approximately one oxygen atom per SnP_2O_7 [23]. The only systematic thermogravimetric investigation of binary, ternary, and quaternary phosphate glasses was carried out by Ouchetto et al. in the temperature range of 1000°C – 1400°C [24, 25]. Figure 1 shows the mass loss of different phosphate-containing glasses at various temperatures, indicating an expected strong dependence on temperature and composition.

A thermodynamic study of the volatilization of $\text{Na}_4\text{P}_2\text{O}_7$ and Na_3PO_4 [26] using Knudsen effusion mass spectrometry revealed the volatilization equations



according to the species recorded in the vapors between 860°C and 1180°C . This means that $\text{Na}_4\text{P}_2\text{O}_7$ volatilizes incongruently, forming Na_3PO_4 as a residue. Na_3PO_4 then sublimates congruently because the sublimation heats of NaPO_3 and Na are equal. Since Na_2O also volatilizes congruently [17] (see Equations 1 and 2), neither sodium nor oxygen accumulates in the molten or solid phase.

In a previous publication, Steblevskii et al. [27] investigated the volatilization of NaPO_3 and observed that the vapor above molten NaPO_3 consists of monomeric NaPO_3 molecules (99.65%) and dimers $(\text{NaPO}_3)_2$ (0.35%). Molecules such as P_4O_6 (gas), P_2O_5 (gas), and P_4O_{10} (gas) could not be detected [26–28].

Thermal analyses in the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{SiO}_2-\text{ZrO}_2$ system did not show any mass loss up to 1200°C [29, 30]. After sintering, the detected phosphorus concentration in the ceramics was very close to the anticipated values. Therefore, the weight losses of the NaSICON material and the $\text{Na}_4\text{Si}_4\text{P}_2\text{O}_{15}$ glass presented in the following sections appear to be associated with pure Na_2O evaporation. Although Na_2O evaporation is examined in the following sections through basic experiments, the discussion of the results will also address its impact on the sintering of NaSICON materials in application-oriented processes.

2 | Experimental

The NaSICON material $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ with an excess of 0.025 mol Na_2O (0.288 wt%; hereafter abbreviated as NZSP) was prepared by solution-assisted solid-state reaction (SA-SSR) as previously described [31]. In brief, stoichiometric amounts of NaNO_3 (99.5%), $\text{ZrO}(\text{NO}_3)_2$ (99%), and $\text{Si}(\text{OC}_2\text{H}_5)_4$ (99%), supplied by VWR International, Belgium, were added to a quartz glass container, and water was used as the solvent. After dissolution of the nitrates, a stoichiometric amount of tetraethyl orthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, was added, followed by a small amount of nitric acid for better dissolution. When the $\text{Si}(\text{OC}_2\text{H}_5)_4$ was hydrolyzed, a corresponding amount of $\text{NH}_4\text{H}_2\text{PO}_4$ was added and stirred for 30 min to form a homogeneous precipitation. The mixture was stirred overnight with 300 rpm at 50°C . The homogenized mixture was first heated from 50°C to 100°C to slowly evaporate the water. The dried solid mixture was then annealed in an oven at 800°C for 3 h to form an amorphous raw powder [32] and to remove gaseous species (H_2O , NO_2 , CO_2). The calcined powder was then ball-milled in ethanol with zirconia balls on a roller bench for 4 days. After drying, the powder was calcined at 700°C prior to the volatilization studies. All thermal treatments were carried out in ambient air. The NaSICON phase was formed during heating to the maximum temperature of the experiments, as verified by the occurrence of a melting point in the differential thermal analysis signal during constant heating up to 1600°C (see below).

To prepare the glass, the reactants (Na_2CO_3 [$> 98\%$, Fluka], SiO_2 [99% , Fluka], and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ [p. a., Merck]) were weighed according to their stoichiometry and ground for 1 h. To produce the melt, the powder mixture was heat-treated in an Al_2O_3 crucible lined with graphite foil in a reducing atmosphere ($\text{Ar}/2\% \text{H}_2$) until it melted. The crucible was heated at a heating rate of 300 K/h to 1250°C for 3 h, cooled to 900°C , and held at this temperature for 1 h. The furnace was then switched off to allow for rapid, free cooling. Part of the glass lump was broken up and ground for the evaporation experiments.

A commercial Na_3PO_4 powder (96%; Aldrich) was used as received. Differential thermal analysis and thermogravimetry (DTA/TG) measurements were carried out with a simultaneous thermal analyzer (STA449F1 Jupiter) from NETZSCH-Gerätebau GmbH (Germany). Al_2O_3 crucibles were used for the experiments. For experiments with NZSP and Na_3PO_4 , the Al_2O_3 crucibles were lined with Pt foil to determine the influence of the

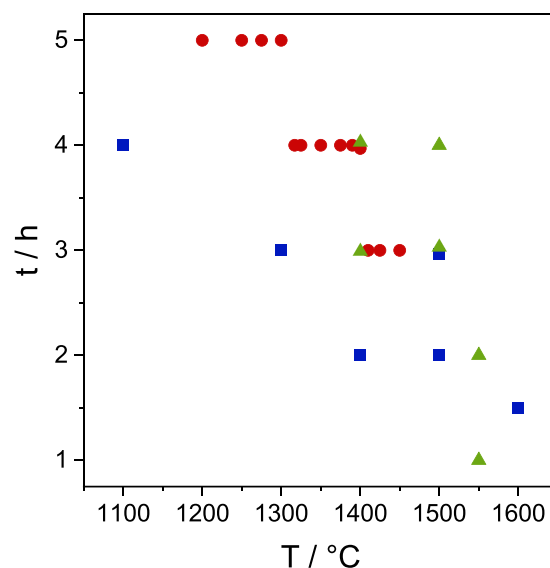


FIGURE 2 | Chosen temperatures and corresponding dwell times for the mass loss measurements of NZSP (red circles), $\text{Na}_4\text{Si}_4\text{P}_2\text{O}_{15}$ glass (blue squares), and Na_3PO_4 (green triangles).

container material. The gas flow of air and Ar was kept constant at 4.2 L/h. A first measurement was performed with a constant heating rate of 600 K/h up to 1600°C , recording the dynamic weight loss during heating. To avoid the influence of adsorbed or chemisorbed water during storage on the measurements, all weight losses at low temperatures ($< 600^\circ\text{C}$) were disregarded. To have a consistent starting point for the measurements, the dynamic curves of weight loss were set to 100% at 600°C .

The weight loss was subsequently measured at different constant temperatures for several hours (see Figure 2). To minimize evaporation loss during heating, all samples were rapidly heated at a rate of 2400 K/h until the chosen temperature was reached. To have a consistent starting point also for the isothermal measurements, the first data point in the isothermal segment was set to 0%.

Since five parameters were varied in this study, a specimen code is introduced here to provide a concise overview of the experimental conditions. Table 1 summarizes the parameters, and the specimen code is defined as “Material-xxxx-y-cr-at,” where xxxx represents the experimental temperature in $^\circ\text{C}$ (Figure 2), y is the dwell time in hours (Figure 2), cr is the material of the crucible, and at is the gas atmosphere used (Table 1).

In selected cases, the Al_2O_3 crucibles were cut lengthwise and polished to determine the interaction of the sample with Al_2O_3 . The polished surfaces were then examined by scanning electron microscopy (SEM) using a GeminiSEM 450 ZEISS scanning electron microscope (Carl Zeiss Microscopy GmbH, Oberkochen, Germany). For the analysis of the elemental distribution, energy-dispersive x-ray spectroscopy (EDS) was performed using an ULTIM MAX 170 energy-dispersive spectrometer from Oxford Instruments. A low voltage was applied to avoid beam damage during scanning.

TABLE 1 | Experimental parameters in this study.

Material	Constant temperature/°C	Dwell time/h	Material of crucible	Gas atmosphere
NZSP	From 1100 to 1600	From 1 to 5	Al ₂ O ₃ (Al)	Air
Na ₄ Si ₄ P ₂ O ₁₅			Pt-lined (Pt)	Ar
Na ₃ PO ₄				

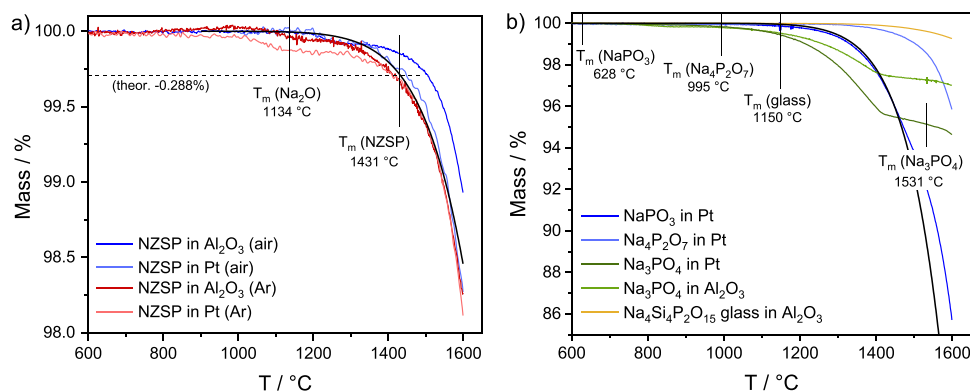


FIGURE 3 | Weight change during constant heating up to 1600°C. (a) Measurements of NZSP with varying crucible materials and gas atmospheres; (b) measurements in air of the sodium phosphates and Na₄Si₄P₂O₁₅ glass. The measurements of Na₃PO₄ (green curves) in Pt and Al₂O₃ show a significantly different weight loss due to a chemical reaction with Al₂O₃. The black lines in (a) and (b) correspond to the fitted data of the measurements with NZSP (in Pt crucible and air atmosphere) and NaPO₃, respectively.

3 | Results

3.1 | Evaporation During Constant Heating

The weight loss of NZSP during heating at a constant heating rate shows similar increasing evaporation rates beginning at about 1200°C (Figure 3a), which is in agreement with previous results [29, 30]. There are minor differences when the crucible material or the gas atmosphere is changed. The measurement curve recorded in Al₂O₃ and air is shifted to higher temperatures by about 50°C, and the melting point is observed at 1405°C instead of 1431°C, as measured in contact with Pt. This indicates a chemical interaction between NZSP and Al₂O₃, which will be discussed in more detail in the next section. Switching from air to Ar revealed a small increase in weight loss between 1100°C and 1300°C, amounting to 0.06% and 0.14% in Al₂O₃ and Pt crucibles, respectively. These small contributions may result from the additional Na₂O during synthesis, but they are much smaller than the expected value (see dashed line in Figure 3a). This can be explained by the fact that the additional Na₂O is incorporated in the NaSICON phase, partially replacing Zr⁴⁺ ions. The partial substitution of Na⁺ ions for Zr⁴⁺ ions on zirconium sites appears to be thermodynamically more stable than full occupancy by Zr⁴⁺ ions [30]. This phenomenon is less pronounced during measurements in air due to the higher oxygen partial pressure (see Equation 4).

According to Figure 3b, the most stable compound in this investigation is the Na₄Si₄P₂O₁₅ glass. During constant heating up to 1600°C, the weight loss only amounts to 0.75%. In comparison, the sodium phosphates show much more pronounced weight losses at lower temperatures. The largest weight loss is observed

for NaPO₃, which evaporates in molecular form. The curve of Na₄P₂O₇ is very similar to that of NaPO₃, but is shifted by 150°C toward higher temperatures. This might be due to a more complex vapor formation via Na₃PO₄ and NaPO₃ (Equations 5 and 6). The mass loss of Na₃PO₄ starts at about 1000°C, followed by a significantly lower rate of mass loss compared to the other two sodium phosphates.

Interestingly, both measurements with Na₃PO₄ show a sudden change in slope at about 1415°C. This reduced volatilization appears to be a material-specific property, whereas the difference in absolute values between both measurements might be related to the interaction between Na₃PO₄ and Al₂O₃ (see Section 4.2).

Assuming that only Na₂O molecules evaporate from NZSP (and NaPO₃ molecules from solid or molten NaPO₃), the partial pressures of Na₂O and NaPO₃ can be used to fit the data in Figure 3 in combination with the simplified Hertz-Knudsen relation [33]:

$$j = \frac{\alpha (p_{\text{eq}} - p_s)}{\sqrt{2\pi MRT}} \quad (7)$$

where j is the molar flux (mol·m⁻²·s⁻¹), α is the volatilization coefficient (an experimental factor varying from 0 to 1), p_{eq} is the equilibrium vapor pressure (Pa), p_s is the vapor pressure on the surface (Pa), M is the molar mass (kg·mol⁻¹), R is the gas constant (J·K⁻¹·mol⁻¹), and T is the absolute temperature (K). Several transformations of the equation, including the extension by the molar mass of Na₂O or NaPO₃, introduction of a reference area (the crucible opening, $S_0 = 29.2 \text{ mm}^2$), and definition of the

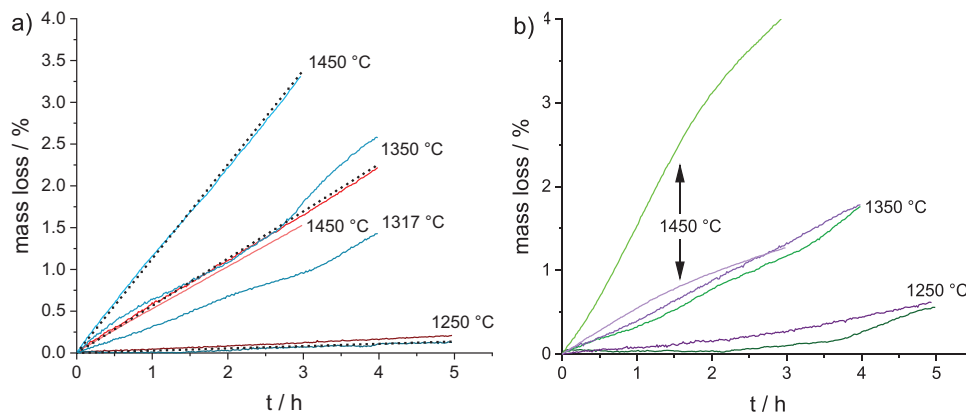


FIGURE 4 | Mass loss from NZSP at different temperatures: (a) in Pt crucibles and in air (turquoise lines) and Ar (red lines), and (b) in Al_2O_3 crucibles and in air (green lines) and Ar (violet lines). The black dotted lines in (a) are the fitted data for the measurements in air using Equations (8) and (9).

constant γ , as outlined in [34], lead to Equation (8):

$$\Delta m = \sqrt{\frac{M}{2\pi R}} \gamma S_0 \int_0^\tau \frac{p_{\text{eq}}}{\sqrt{T}} d\tau \quad (8)$$

where τ is the time (s). The equilibrium vapor pressure p_{eq} of Na_2O was taken from the investigation of Piacente et al. [17] as:

$$\log(p_{\text{eq}}/Pa) = 10.49559 - 11920/T \quad (9)$$

whereas the equilibrium vapor pressure p_{eq} of NaPO_3 was taken from [27] and is applied in Figure 3b:

$$\log(p_{\text{eq}}/Pa) = 12.52476 - 15030/T \quad (10)$$

The resulting fitted curves are shown in Figure 3 as black lines and were obtained with $\gamma = 3.6 \times 10^{-8}$ and 7.7×10^{-8} for the measurement of NZSP (in a Pt crucible and air atmosphere) and NaPO_3 , respectively. In the latter case, a deviation between the measured and fitted curves at $T > 1475^\circ\text{C}$ can be observed, which is likely due to the hindered removal of vaporized molecules from the crucible.

3.2 | NZSP

3.2.1 | TG Measurements

The mass loss of NZSP increases linearly over time (Figure 4a). The rate of mass loss increases significantly from 0.04%/h at 1250°C to 0.55%/h at 1350°C and 1.1%/h at 1450°C . There are only two deviations from this general trend: (1) the sample NZSP-1350-4-Pt-air shows a second, increased rate of mass loss at around 2.75 h, and (2) the sample NZSP-1450-3-Pt-Ar reveals a rate of mass loss of only 0.51%/h, approximately half of the value measured in air. Whereas the first deviation remains unresolved, the latter deviation appears to be systematic, since the same reduced rate of mass loss was also obtained for measurements in Al_2O_3 crucibles. This indicates that vaporization is strongly inhibited under these specific experimental conditions (1450°C , Ar), which is likely due to the saturation of the gas space in the crucibles, that is, not eliminated by the applied gas stream.

The measurements with NZSP in Pt crucibles and in air were also fitted with Equations (8) and (9) (black dotted lines in Figure 4a), with $\gamma = 2 \times 10^{-8}$, 1.4×10^{-7} , and 1.08×10^{-7} for the data at 1250°C , 1350°C , and 1450°C , respectively. A very good agreement with the measurements is obtained as long as the evaporation curves do not deviate from linearity.

The measurements in Al_2O_3 crucibles (Figure 4b) show some remarkable differences. First, the measurements in air show two or even three slopes. Second, compared with the measurements in Pt crucibles, the mass losses are higher at 1250°C and 1450°C , but are lower at 1350°C (Figure 4a). This irregular behavior can be explained by the fact that NZSP reacts with the Al_2O_3 crucible and forms melts at the applied temperatures. At 1150°C , no mass loss was measured. Therefore, this result is not shown in Figure 4b. However, even at this temperature, a strong reaction with the crucible and decomposition of the sample were observed in subsequent SEM investigations.

3.2.2 | SEM Investigations

After determining the mass loss, the remaining specimens in the crucibles were characterized by electron microscopy. Figure 5 compares NZSP after thermal treatment in air using Pt crucibles (Figure 5a–c) and Al_2O_3 crucibles (Figure 5d–f). The observations made with the samples in Pt crucibles reflect the typical and expected behavior at different temperatures: At 1250°C , sintered agglomerates are visible. The large grains are homogeneous and contain several small ZrO_2 grains (white dots in Figure 5a), which typically appear after sintering of this NZSP composition [16, 30]. No gradient of Na across the agglomerates was detected by EDS. The sample heat-treated at 1350°C also shows strongly sintered agglomerates, with large grain growth and numerous microcracks due to thermal expansion anisotropy [35]. In addition, the ZrO_2 grains are slightly enlarged, and some local glass formation can be observed (small dark gray regions in Figure 5b). Again, no Na gradient was detected across the agglomerates. After the dwell time at 1450°C , the sample is molten and decomposed. At least four phases were identified: ZrO_2 , glass, Na_3PO_4 , and residual NZSP. This incongruent melting is expected, since a signal was recorded at 1430°C during the simultaneous DTA measurement.

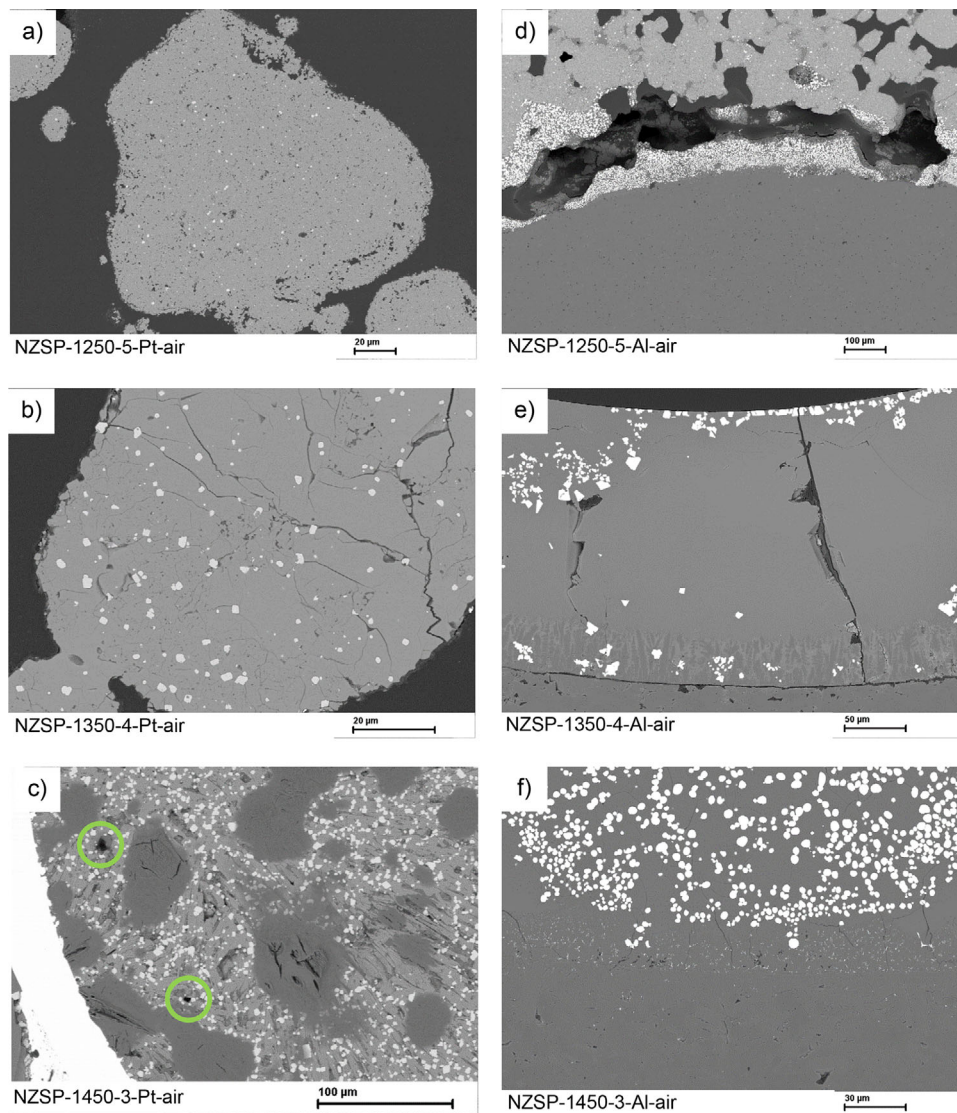


FIGURE 5 | SEM images with back-scattered electrons (BSEs) of polished NZSP cross sections after measurements (a–c) in Pt crucibles and (d–f) in Al_2O_3 crucibles at different temperatures.

The remaining pores (black areas within the green circles in Figure 5c) indicate the internal pathways for Na_2O evaporation from the depth of the sample close to the Pt foil (white band on the left).

In contrast to the above observations, the use of Al_2O_3 crucibles leads to significant interactions with NZSP. In addition to strongly sintered agglomerates with local glass formation and ZrO_2 grains at the top of Figure 5d, a strong reaction and decomposition of NZSP can be observed at the interface due to the precipitation of ZrO_2 in a reaction zone of about 100 μm . After exposure at 1350°C (Figure 5e), the sample is molten but much more homogeneous, with only enlarged ZrO_2 grains. Evidently, the diffusion of alumina into NZSP leads to a substantial decrease in the melting temperature, prior to the detected DTA signal at 1405°C, and to the formation of a glassy constitution. At the interface with the Al_2O_3 crucible, a strong reaction and interdiffusion can be observed, with a visible reaction zone of about 50 μm . Similarly, after heat treatment at 1450°C (Figure 5f), the NZSP is molten and decomposed, with a larger number of circular ZrO_2 grains in the

glassy bulk and precipitation of small Zr-containing particles in a reaction zone with alumina of about 20 μm .

Despite their very different microstructures, the NZSP samples exhibit only minor differences in terms of mass loss. Nevertheless, the SEM images help to explain the minor differences: (1) The TG measurements at 1250°C showed an increased slope of sample NZSP-1250-5-Al-air starting after 3.5 h (Figure 4b). Figure 5d suggests that this may be due to the decomposition of NZSP, with the released Na_2O contributing to increased evaporation after a certain reaction time (incubation time). (2) Measurements at 1350°C indicate that the rates of mass loss are lower with Al_2O_3 crucibles than with Pt crucibles. The reason for this appears to be the difference in surface area: whereas Figure 5b still shows agglomerates, the sample in Figure 5e is a nearly homogeneous melt with a very limited surface area and, therefore, a reduced evaporation rate. (3) The mass loss at 1450°C in air results in the highest evaporation rates: 1.1%/h and 1.6%/h for the measurements with the Pt crucible and the Al_2O_3 crucible (initial 1.5 h, Figure 4), respectively. This difference can only be attributed

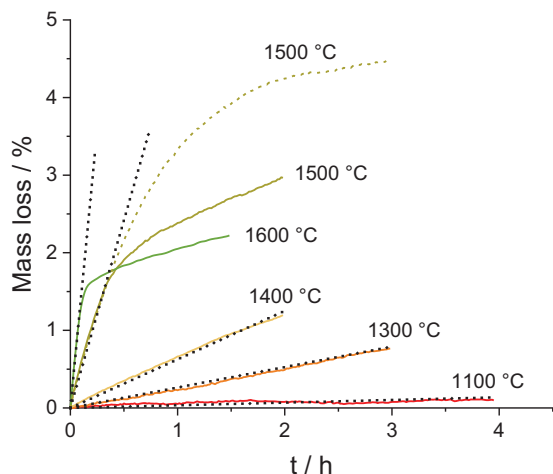


FIGURE 6 | Mass loss from $\text{Na}_4\text{Si}_4\text{P}_2\text{O}_{15}$ glass at different temperatures. The short-dashed line represents a measurement in a Pt crucible instead of the Al_2O_3 crucible used for the other measurements. The black dotted lines represent fitted data obtained using Equations (8) and (9).

to the different morphology of the two molten samples, that is, the higher fraction of the glass phase in sample NZSP-1450-3-Al-air.

3.3 | Glass $\text{Na}_4\text{Si}_4\text{P}_2\text{O}_{15}$

3.3.1 | TG Measurements

The mass loss at constant temperatures shows continuous changes with increasing temperature. At 1100°C , the only measuring temperature below the melting point of the glass, the mass loss is very low and close to the detection limit of the thermobalance. Despite the very small fluctuations observed during the measurement, the volatilization rate can be assumed to be very low and constant, as it is for the measurement at 1300°C within the chosen dwell time (Figure 6). The measurement at 1400°C indicates a first deviation from a constant volatilization rate starting at about $t = 1.5$ h and tending toward a decreasing rate. This change in slope is much more pronounced for the measurements at 1500°C and 1600°C . With increasing temperature, the decrease in the volatilization rate begins at earlier measuring times and converges toward the rate observed at 1300°C and 1400°C . Hence, two processes can be distinguished, but the linear plot of the data already suggests that there is no logarithmic or parabolic dependence.

In order to determine the reason for the two evaporation rates, the measurement at 1500°C was repeated but stopped after 15 min, and an additional measurement was carried out with a Pt crucible (Figure 6). In the latter case, the same initial slope was obtained, and the final slope is very similar to that of the measurement in an Al_2O_3 crucible. It is only the transition between the two processes that requires more time.

3.3.2 | SEM Investigations

The sample of the aborted measurement and the sample exposed to 1500°C for 2 h were analyzed using SEM/EDS. The sample

with the shorter dwell time exhibited a reaction zone of 10–20 μm (Figure 7a), which could be distinguished from the rest of the glass by its different grayscale. Several EDS measurements were performed from the Al_2O_3 /glass interface into the bulk glass to determine the elemental concentration gradients. The most notable result was the dissolution of Al_2O_3 from the crucible into the glass. After 0.25 h, the diffusion zone had a thickness of about 100 μm (Figure 7b). The sample exposed for 2 h also exhibited a gradient within the first 100 μm ; however, a high and near-constant Al_2O_3 content was then observed, which cannot be explained by diffusion alone.

For the present case, in which a medium provides a species with an initial concentration c_0 on its surface (at $x = 0$) and the concentration of this species in an adjacent medium is $c = 0$ at $t = 0$, the following solution of Fick's second law can be applied:

$$c(x, t) = c_0 - c_0 \operatorname{erf}\left(x/\sqrt{Dt}\right) \quad (11)$$

where D is the diffusion constant of the species under consideration (here Al^{3+} ions or Al_2O_3 in general), x is the distance from the Al_2O_3 /glass interface, and erf is the error function. The experimental data were fitted using the parameters $c_0 = 16$ at%, $D = 5 \times 10^{-9}$ cm^2/s , $t_1 = 0.25$ h = 900 s, and $t_2 = 7200$ s to obtain the gray and black dashed lines in Figure 7b, respectively. The gray curve reflects the measured EDS data very well, whereas the black line only agrees with the measurements within the first 100 μm . For larger distances from the Al_2O_3 /glass interface, the nearly constant Al concentration in the glass suggests an additional homogenization process, such as convection, in the melt. The assumption that the two volatilization rates are caused by the Al_2O_3 content in the melt—due to a change in viscosity, for example—is contradicted by the experiment with the Pt crucible. Here, too, similar evaporation rates occur, although the transition is spread over time and no Al_2O_3 is present.

3.4 | Na_3PO_4

3.4.1 | TG Measurements

The mass loss of Na_3PO_4 is much higher than the two other materials at the same temperature. The measurements at 1400°C and 1500°C still show moderate values and sublimation rates of 0.94%/h and 1.58%/h, respectively. However, the measurement at 1550°C , at which temperature the sample is in a molten state, shows exceptionally high mass loss and an evaporation rate of 35.7% between 1 and 1.5 h of the dwell time (Figure 8a). In addition, the measurements at 1400°C and 1500°C exhibit two apparent slopes, whereas the measurement at 1550°C shows three slopes during the measurement period. The pronounced mass losses can be linked to a different volatilization mechanism and the evaporation of NaPO_3 (Equation 6).

Measurements in Al_2O_3 crucibles (Figure 8b) show a rather different picture: (1) sublimation at 1400°C is reduced compared to the measurement in a Pt crucible; (2) at 1500°C , the opposite occurs, with a strong parabolic increase in mass loss; and (3) evaporation at 1550°C is again almost linear and much lower than in a Pt crucible. These remarkable, non-systematic deviations from the measurements in Pt crucibles are the consequence of

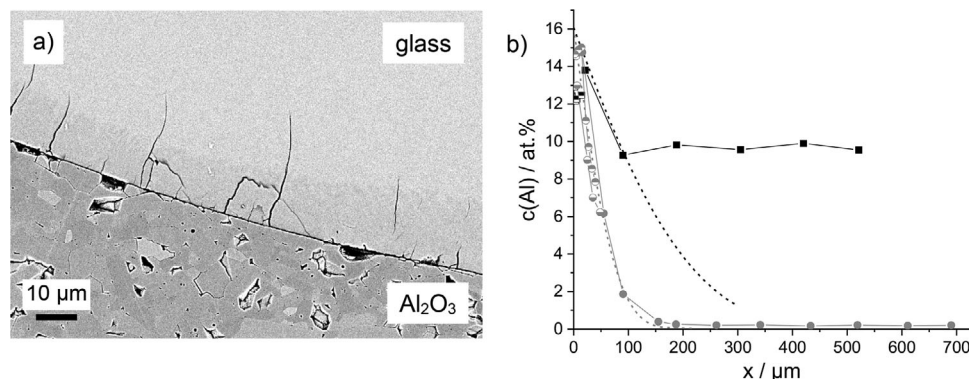


FIGURE 7 | (a) BSE-SEM image of the Al_2O_3 /glass interface after 0.25 h at 1500°C. A diffusion zone of 10 μm is clearly visible in the glass due to its darker shade of gray. The microcracks in the glass likely formed during cooling of the melt. (b) Diffusion profiles of Al^{3+} ions after 0.25 h (gray) and 2 h (black) at 1500°C. The half-filled symbols indicate additional measurements at different positions. The dashed lines represent the fitted curves according to Equation (11) (see text).

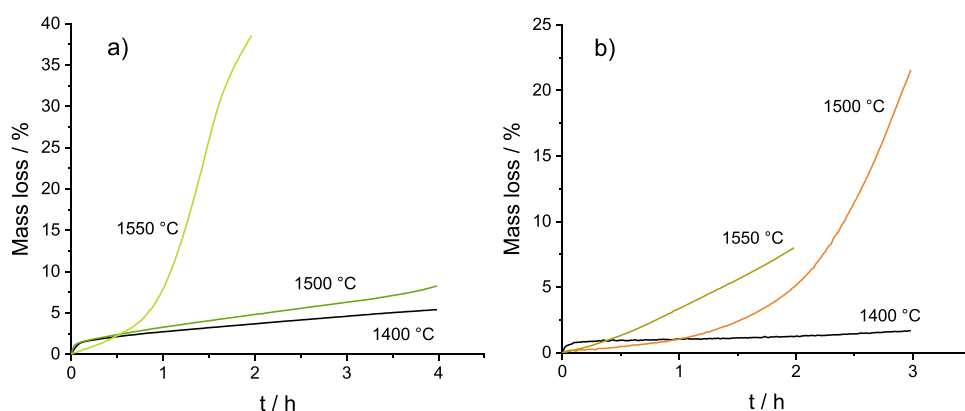


FIGURE 8 | Mass loss from Na_3PO_4 in air at different temperatures: (a) in Pt crucibles and (b) in Al_2O_3 crucibles.

strong reactions between Na_3PO_4 and Al_2O_3 already at 1400°C, as described in the following section.

3.4.2 | SEM Investigations

The interaction between Na_3PO_4 and Al_2O_3 is already very pronounced at 1400°C (Figure 9a), with an apparent reaction zone of approximately 150 μm . However, the elemental distribution is not homogeneous, and no diffusion gradient was observed using EDS line scans. To gain insight into the reaction products, a series of EDS point analyses was recorded at several positions along the interface, as exemplified in Figure 9a by the yellow line along which 25 analyses were performed. In this way, a statistical scatter of the elemental distribution was collected and inserted in the ternary phase diagram (Figure 9b). Although the data points show a large scatter, some general trends can be recognized:

- All data points fall within a triangle formed by the corners of Al_2O_3 , NaPO_3 , and Na_2O
- The reaction products at 1400°C accumulate along the tie line $\text{Na}_5/\text{Na}11\text{-N}3\text{P}$ (i.e., between the β -aluminas and Na_3PO_4) and around the initial composition Na_3PO_4

- The reaction at 1500°C is more pronounced, and the elemental distribution fills the entire triangle
- At 1550°C, the reaction products again accumulate along the tie line $\text{Na}_5/\text{Na}11\text{-N}3\text{P}$, but much closer to the Al_2O_3 -rich area

4 | Discussion

4.1 | General Remarks

In the investigated time–temperature window, the mass loss of NZSP and $\text{Na}_4\text{Si}_4\text{P}_2\text{O}_{15}$ amounts to a few percent, whereas values of up to 40% are observed for Na_3PO_4 . This significant difference can be explained by the different thermodynamics of Na_3PO_4 volatilization, which involves NaPO_3 molecules in addition to Na_2O . Since vapor pressure is highly dependent on the solid or liquid material with which it is in equilibrium [36], the measurements here reflect the different evaporation behaviors of NZSP and $\text{Na}_4\text{Si}_4\text{P}_2\text{O}_{15}$. Therefore, there can be no universal interpretation of the results. However, in general, when selecting a crucible material, both the experimental parameters and the sample under investigation must be considered. The use of alumina crucibles in DTA/TG measurements is common practice, but it is not recommended for alkali-containing materials, as

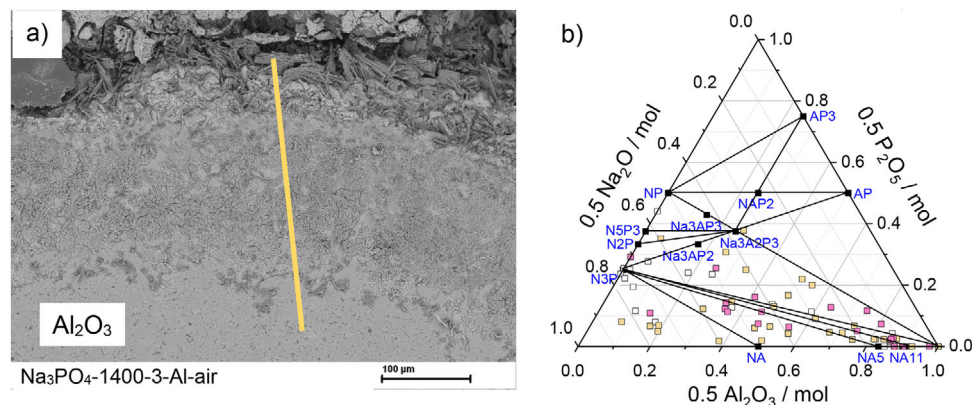


FIGURE 9 | (a) Polished cross section of the $\text{Na}_3\text{PO}_4/\text{Al}_2\text{O}_3$ interface after measurement at 1400°C . The yellow line indicates the position of 25 consecutive EDS point analyses. (b) Ternary phase diagram showing the elemental distribution after measurements at 1400°C (white squares), 1500°C (yellow squares), and 1550°C (pink squares). The blue abbreviations indicate the atomic ratios of the existing compounds (e.g., AP = AlPO_4 , N2P = $\text{Na}_4\text{P}_2\text{O}_7$).

reported here. Even brief contact times can cause severe contamination or even decomposition of the sample, compromising the measurement results. As a practical recommendation, DTA/TG measurements on alkali-containing materials should always be performed with a Pt-lined crucible.

It is worth noting that the synthesis method may have an impact on Na_2O evaporation. Since NZSP has been prepared in many different ways [31], it is important to distinguish between methods in which the starting materials are first dissolved (SA-SSR as applied here, sol-gel approaches, combustion methods, precipitation reactions) and those that use solid starting materials (solid-state reaction, reactive sintering). In the former methods, the starting materials can be chosen freely, provided they can be dissolved and processed into the desired liquid starting mixture. This generally results in an atomic mixture of ions and in amorphous or nanocrystalline raw powders that exhibit high sintering reactivity. In contrast, for the latter methods, the choice of starting materials and their quality (particularly the particle size distribution) are crucial for a successful synthesis. In the case of a solid-state reaction, multiple grinding and tempering steps are necessary to obtain a single-phase product, due to undesirably large particle sizes and poor contact between the particles. If the feedstocks contain very coarse-grained sodium-containing materials, Na_2O evaporation may vary significantly depending on the starting material and may not be comparable to the data presented here. Typically, the tempering steps and sintering are carried out at higher temperatures than those used for the calcination and sintering of powders prepared from liquid-phase mixtures. Therefore, powders produced by solid-state reactions tend to exhibit higher losses of Na_2O than powders that can be sintered at lower temperatures. When producing powders from liquid mixtures, the methods themselves—as well as variations in quality within a single method—can result in sintering temperatures ranging from 1100°C to 1350°C being necessary to obtain nearly dense NZSP samples. For such powders, the evaporation curves shown here should be universally applicable for estimating the Na_2O evaporation.

The measurements with NZSP clearly show that the mass loss at 1250°C , a typical sintering temperature of such ceramics, is

very low (Figures 3a and 4). At $\Delta t = 4$ h (Figure 4a), the mass losses are 0.11% and 2.25% at 1250°C and 1350°C , respectively. This corresponds to the release of 1.8 and 36.3 mmol Na_2O from the solid samples, which is equivalent to 0.19 g and 3.8 g Na_2CO_3 , respectively that need to be added to the initial synthesis mixture of 1 mol NZSP. Depending on the chosen sintering temperature and dwell time, the required amount of additional sodium source can be interpolated, extrapolated, or calculated using Equation (8). In general, the additions reported in the literature are often higher and only rarely meet the amount of sodium source necessary to compensate for the mass loss. Since the data collected here are only representative for measurements performed in a thermobalance, they should only be used as a rough estimate. For practical applications, the mass loss should be determined in a real environment (type of sample, type of sintering specification as described in Section 4.3, type of furnace or heating equipment).

As long as the thermochemistry and the partial pressure of the volatile species have been well investigated, the mass loss can be estimated using Equation (8) for both constant heating and isothermal experiments. However, in some cases, the expected constant volatilization rate is disturbed by a change in the evaporation kinetics and, more frequently, by a reaction with the Al_2O_3 crucible. As mentioned above, although reactions with the investigated materials were anticipated, the intensity of the reactions was underestimated. Therefore, volatilization experiments with alkali-containing powders should be carried out using a Pt lining.

4.2 | Activation Energies

The mass loss, Δm , can be expressed as:

$$\Delta m = b + k\Delta t \quad (12)$$

with $b = 0$ for the initial volatilization rate. The slopes, k , of selected curves at different temperatures in Figures 4, 6, and 8 were plotted in an Arrhenius diagram (Figure 10a) to deter-

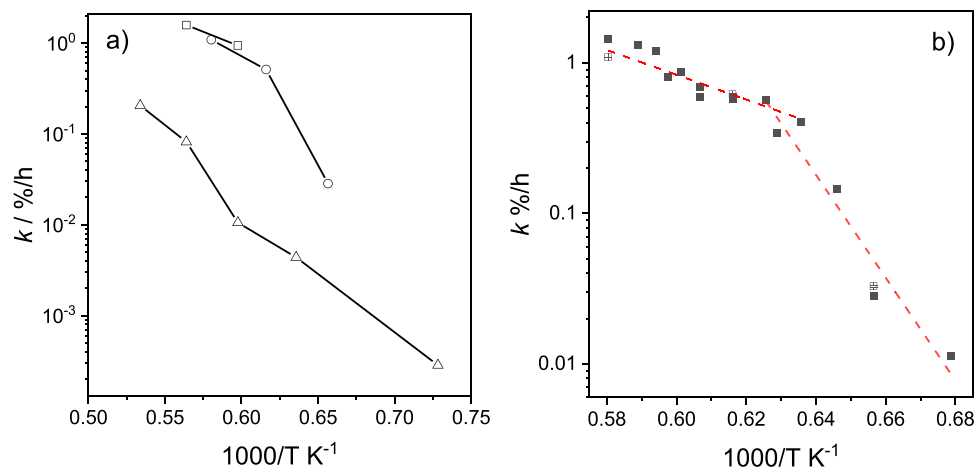


FIGURE 10 | (a) Volatilization rates, k , of NZSP (circles), $Na_4Si_4P_2O_{15}$ (triangles), and Na_3PO_4 (squares) for the measurements shown in Figures 4a, 6, and 8a. (b) Additional measurements with NZSP for a more accurate determination of the activation energy between 1200°C and 1450°C. The three data points shown in (a) are indicated here as open symbols with error bars (smaller than the symbol size). The red dotted lines are linear regressions of the data in the temperature intervals of 1200°C–1325°C and 1300°C–1450°C.

TABLE 2 | Activation energies (in kJ/mol) determined from the evaporation rates in Figure 10.

Material	Crucible	Gas	ΔT	E_a /kJ mol $^{-1}$
NZSP	Pt	Air	1200°C–1325°C	654 ± 64
NZSP	Pt	Air	1300°C–1450°C	158 ± 16
$Na_4Si_4P_2O_{15}$	Al_2O_3	Air	1100°C–1600°C	283 ± 24
Na_3PO_4	Pt	Air	1400°C–1500°C	127

mine the activation energies (E_a) of the volatilization processes (Table 2).

In three cases, analysis of the slopes of the four sets of measurements with NZSP revealed a significant deviation from linearity in the Arrhenius diagram, with a significantly lower slope measured at 1450°C. As mentioned above, volatilization is strongly inhibited at 1450°C using Ar atmosphere. This also appears to be the case for the other measurements at 1450°C, with the exception of those performed in an Al_2O_3 crucible and air. The set of measurements in Pt and air also shows a lower slope than expected at 1450°C.

Additional measurements (see Figure 2) were therefore performed to determine E_a with greater accuracy. These additional measurements revealed two different temperature regimes, allowing a more precise determination of E_a (Figure 10b and Table 2). The $Na_4Si_4P_2O_{15}$ glass shows a relatively consistent change in the initial slope (Figures 6 and 10a), resulting in an E_a of 283 ± 24 kJ/mol. The measured mass losses of Na_3PO_4 are impeded by the measurement at 1550°C, at which temperature the material is molten. This change of state clearly has a significant impact on the volatilization rate. Considering only the data obtained at 1400°C and 1500°C, and excluding the first 0.25 h of each measurement, the change in slope between the two measurements results in an E_a of 127 kJ/mol. Although the activation energy of Na_3PO_4 should be regarded as a provisional

approximation, it is the lowest E_a value among the three materials, followed by the high-temperature E_a of NZSP and that of $Na_4Si_4P_2O_{15}$ glass.

4.3 | Implications for the Manufacturing of NaSICON Components

To achieve high energy densities in battery cells using solid electrolytes, such as the NaSICON materials, the separator should be as thin as possible. With the tape casting method, layer thicknesses of 20–200 μm can be easily achieved [37], and initial reports demonstrate the impact of layer thickness on battery performance [38]. However, there are several challenges that still need to be addressed during component manufacturing, especially for tape-cast layers:

1. The depletion of sodium oxide at the component surface
2. The bending, warpage, or cracking of the sintered bodies
3. The choice of materials for sintering supports

The first point is particularly crucial for tape-cast layers, as the evaporation of Na_2O can not only lead to the decomposition of NaSICON and pronounced ZrO_2 formation at the surface (Figure 11a), but also to warpage of the sintered layers. The evaporation of Na_2O is less critical for thick components like pellets, since the decomposed region can be polished away. However, the reduced thickness of the tape-cast sheets means that this mechanical treatment is not a viable solution. One option to mitigate Na_2O depletion is the sintering of NaSICON materials in a Na_2O -rich atmosphere.

Similar approaches have also been adopted in the manufacture of β -alumina ceramics: (1) encapsulation of pressed pellets in Pt foil [39]; (2) coverage of pellets with powders of the same composition [40]; (3) enclosure of green tubes in magnesia crucibles to maintain Na_2O [41]; (4) application of a two-step sintering procedure in a buffer of β -alumina/ Na_2CO_3 powder [42].

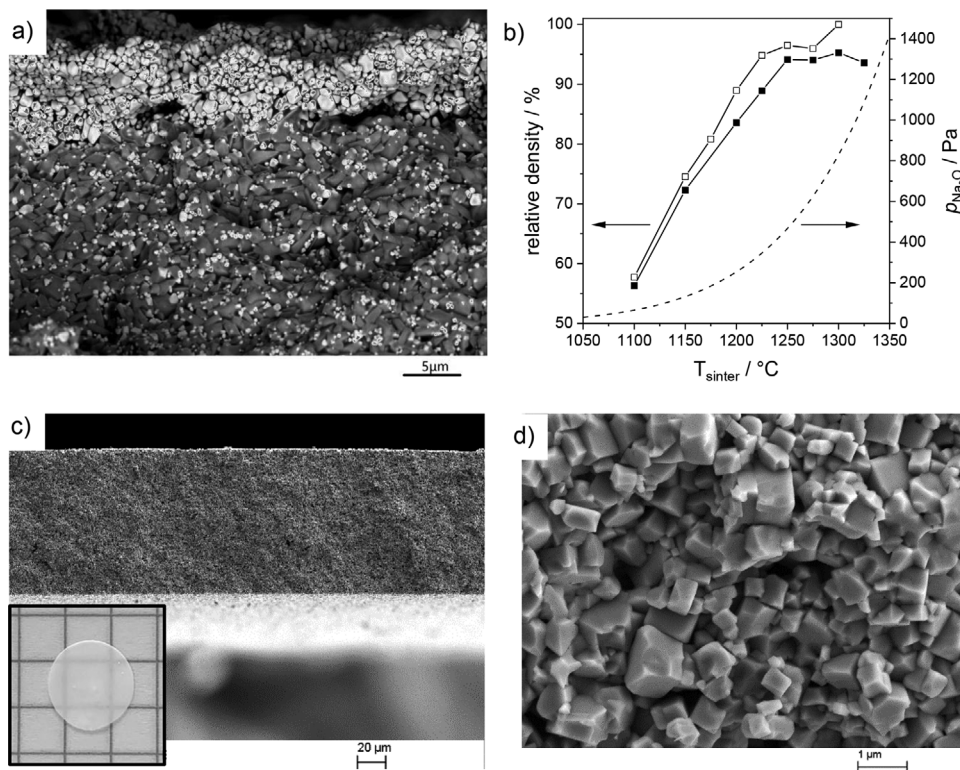


FIGURE 11 | (a) Fracture surface of a conventionally sintered NaSICON tape (1265°C for 3 h) without surface protection, with the upper surface exposed to the furnace. The white particles are ZrO₂ grains. (b) Relative density of NZSP samples sintered at different temperatures in air (filled symbols) and in a saturated Na₂O atmosphere (open symbols). The dashed line corresponds to Equation (9). (c and d) Secondary electron SEM images of fracture surfaces of a NaSICON tape after sintering at 1265°C for 4 h between two NaSICON plates. In (c), the digital image in the bottom left shows a translucent NaSICON tape (9.9 mm in diameter), demonstrating its excellent quality.

Such approaches have also been reported for Li⁺ ion conductors [43 and references therein]. In the present study, we used Na₂CO₃ powder placed in an alumina crucible alongside pressed green pellets and covered with a large alumina crucible placed upside down. This setup allows for sintering to be performed easily in a saturated Na₂O atmosphere, improving the quality of the ceramics compared with conventionally sintered bodies. As an example, in accordance with Equation (9), encapsulation delivers a partial pressure of 467 Pa at 1250°C. Figure 11b shows the difference in densification for the two sets of samples sintered with and without encapsulation.

For ceramics, the sintering process is a key processing step in component manufacturing and is directly related to the microstructural changes that occur in the material (e.g., densification, grain growth, crystallization), which in turn affect the electrical and electrochemical properties. So far, for temperatures above 1000°C, replacing Pt foil as the only viable sintering support for NZSP ceramic tapes has transpired to be very difficult, because all typical refractory oxides react with NZSP. To the best of our knowledge, there are no specialized supports that can be used. To prevent a strong reaction with refractory oxides, sintering is often carried out in a powder bed of NZSP between the NZSP specimen and the setter. In this way, the sintered body is protected at the expense of the powder, which reacts with the substrate. Covered with a crucible, the powder bed also serves as a source of Na₂O during sintering [37, 44, 45].

To avoid the use of Pt foils as the state-of-the-art sintering base, it is necessary to identify materials compatible with NZSP and to develop a new method. This method must vary not only the sintering parameters (temperature, time, heating rate), but also the sintering arrangement, that is, the application of ceramic disks used as sintering supports and covers during the sintering process.

Three different NaSICON sintering support compositions were therefore prepared: Na_{3.4}Zr₂Si_{2.4}P_{0.6}O₁₂, Na_{3.8}Zr₂Si_{2.8}P_{0.2}O₁₂, and Na₄Zr₂Si₃O₁₂. Silicate-rich NaSICON materials have already been reported to have high melting points [46], which is why they were considered promising candidates for the development of a temperature-stable sintering support. Initially, the powders of the sintering supports were uniaxially pressed to a diameter of 35 mm and later to 126 mm, with a thickness of 2–2.5 mm in both cases. The prepared NaSICON pellets were sintered at 1300°C for 4 h.

After sintering, the Na₄Zr₂Si₃O₁₂ substrates were highly porous and brittle. In addition, when a tape-cast specimen with a diameter of 13 mm was placed between two substrates, no shrinkage of the sintered tapes was observed, and the samples were fragile and frequently exhibited crack formation. The quality of the sintered Na_{3.8}Zr₂Si_{2.8}P_{0.2}O₁₂ substrates was slightly better in terms of porosity and brittleness; however, no shrinkage of the tape-cast samples was observed in this case either. The rough surface of these two substrate types clearly appears to inhibit the shrinkage and densification of the NZSP tapes.

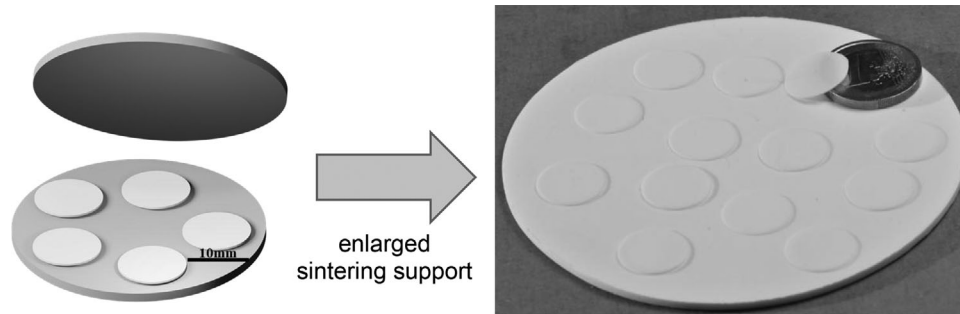


FIGURE 12 | Left: schematic illustration of NZSP tape-cast thick films sandwiched between sintering plates. Right: photograph of sintered dense NZSP tapes (10.5 mm in diameter) on an NZSP plate with a diameter of 126 mm.

In contrast, the use of the $\text{Na}_{3.4}\text{Zr}_{2.4}\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ substrates yielded very satisfactory results. When NZSP green tapes were sandwiched between two sintered plates, the specimens exhibited improved densification, with a high relative density of more than 95%, as determined by the Archimedes method. The SEM images of the fracture surface in Figure 11c,d clearly show the high relative density of the NZSP tapes and are therefore in good agreement with the calculated density. The inset image in Figure 11c shows the improved flatness of the sintered tapes, indicating that the direct load exerted by the upper NZSP plate positively contributed to limiting the possible deformation of the NZSP tapes during the sintering process. The flatness of the tapes, and the fact that the two NZSP plates create a nearly enclosed environment during the sintering process, enabled ionic conductivity measurements to be performed. These measurements resulted in values of $(1.15 \pm 0.1) \times 10^{-3} \text{ S/cm}$ at room temperature, which are in agreement with the values reported in [38] and indicate that no accumulation of ZrO_2 impurities blocks ionic transport.

This approach was found to be reproducibly efficient and effective in increasing the relative density and in minimizing the possibility of bending, warpage, crack formation, and deformation of sintered NZSP tapes, especially when sintering at high temperatures. Increasing the size of the sintering substrates to 126 mm yielded similarly good results (Figure 12) and demonstrates that this new technique for sintering green ceramic tapes provides a versatile platform for producing NaSICON thick films. It also opens a route for producing other promising ceramic, alkali-containing, tape-cast layers.

5 | Conclusions

The fast ion conductor $\text{Na}_{3.4}\text{Zr}_{2.4}\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ was chosen as a model substance to investigate the evaporation of Na_2O at high temperatures and to estimate the mass loss during sintering of this material. Typical sintering temperatures for NZSP vary between 1250°C and 1300°C, and the obtained rate of mass loss ranged from 0.03%/h to 0.4%/h, yielding values of 0.12 to 1.6 wt% after 4 h. This range is significantly lower than the amounts of sodium additives often used to compensate for an expected weight loss and explains, at least in part, the significant differences in the reported conductivity data.

In addition to NZSP, the $\text{Na}_4\text{Si}_4\text{P}_2\text{O}_{15}$ glass and crystalline Na_3PO_4 were chosen to investigate the impact of the physical state and the volatilization mechanism on the evaporation of Na_2O . In the case of $\text{Na}_4\text{Si}_4\text{P}_2\text{O}_{15}$, the measured mass losses were in the same range as those of NZSP. Below 1300°C, however, the activation energy of the Na_2O evaporation process was significantly lower than that of NZSP, namely 283 kJ/mol and 654 kJ/mol, respectively. However, above 1300°C, NZSP showed a much lower activation energy of 158 kJ/mol, which is comparable to that of Na_3PO_4 . The orthophosphate exhibited significantly higher mass losses, especially in the molten state at 1550°C, which can be attributed to the congruent evaporation of NaPO_3 and Na_2O .

Based on these findings, several recommendations can be made: (1) Evaporation tests or routine DTA/TG measurements with alkali-containing substances should always be carried out in crucibles with a Pt lining to avoid reactions with the commonly used Al_2O_3 crucible material; (2) to determine the correct amount of sodium addition, the mass losses determined here can be adapted to the relevant sintering parameters. However, it is highly advisable to determine the mass loss under real sintering conditions before processing the target composition; and (3) to prevent mass loss during sintering, heat treatments in a Na_2O -containing atmosphere can also be considered, or sintering aids made from the same material can be used as covers and setters for the sintered bodies.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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