

Niobium diffusion in niobium-doped titanium dioxide

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Abstract The present work studied the self-diffusion coefficient of ^{93}Nb in Nb-doped TiO_2 single crystal (4.3 at.% Nb) at high oxygen activity [$p(\text{O}_2)=21$ kPa] over the temperature range 1,073 to 1,573 K. The diffusion-induced ^{93}Nb concentration profile was determined by using secondary ion mass spectrometry (SIMS). The subsequently determined self-diffusion coefficient of ^{93}Nb exhibits the following temperature dependence: $D_{^{93}\text{Nb}} = 1.77 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \exp\left(\frac{-197 \pm 9 \text{ kJ mol}^{-1}}{RT}\right)$. This study builds upon a similar study performed previously for ^{93}Nb tracer diffusion in undoped TiO_2 , and identifies the effect of compositional change on self-diffusion behaviour. The obtained activation energy has been considered in terms of migration and formation enthalpies of titanium vacancies.

Keywords Titanium dioxide · Diffusion · Doping · Secondary ion mass spectrometry · Niobium · Photoelectrodes

Introduction

Interest in titanium dioxide, TiO_2 , has steadily grown since 1972 when Fujishima and Honda [1] first demonstrated that illuminated TiO_2 could photoelectrochemically split water. This represented an outstanding opportunity to generate clean and abundant fuel in the form of hydrogen. The theoretical basis behind photoelectrochemical water splitting has been mainly developed by Bockris and his coworkers [2–4]. Recently, the interest in TiO_2 has steadily intensified due to its wide range of environmentally friendly applications, including water and air purification [5, 6], self-cleaning surfaces [5] and super-hydrophilic coatings [5].

Whilst the number of potential applications for TiO_2 is growing, the need to modify the properties of TiO_2 in order to enhance its performance is also growing. This need may be addressed by changing the chemical composition of TiO_2 through the incorporation of aliovalent ions leading, in consequence, to subsequent changes to its functional properties.

Doping has been widely applied for the modification of TiO_2 [7–9]. However, this approach may only lead to well-defined specimens when the transport kinetics of the dopant ions in TiO_2 are well-known. Knowledge of the related diffusion data enables the prediction of the processing conditions required for the homogeneous distribution of the dopant within the specimen. In the case where the diffusion kinetics are not known, then the homogeneous distribution of the dopant cannot be reliably assumed. The investigated properties cannot then be considered as representative of the material, but represent the specific processing history instead. Frequently, this is insufficiently reported to enable reproduction and confirmation by other investigators.

The present work is dedicated to Professor John Bockris on the occasion of his 85th birthday. His contribution to the progress of modern electrochemistry is well-known to several generations of students and researchers who have been using his textbooks. His specific contribution to the theory of photoelectrochemical water splitting is known to all working in this fascinating area.

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The authors of the present work have recently determined the ^{93}Nb tracer diffusion in undoped TiO_2 single crystal over the temperature range 1,073–1,573 K and at high oxygen activity [$p(\text{O}_2)=21$ kPa] [10]. An activation energy of 244 kJ mol^{-1} was determined. In the present work, the self-diffusion of ^{93}Nb in Nb-doped TiO_2 will be similarly investigated under identical conditions of temperature and oxygen activity. The aim of the present work is to determine the effect of composition on the temperature dependence of the ^{93}Nb self-diffusion coefficient for Nb-doped TiO_2 . It is expected that comparison of the diffusion data for undoped TiO_2 and Nb-doped TiO_2 will enable the assessment of the effect of bulk composition on the self-diffusion of ^{93}Nb . The effect of Nb on the properties of TiO_2 could be considered in terms of the concentration of Ti vacancies, which are formed during the incorporation of Nb. Therefore, the effect of Nb on the diffusion kinetics could be considered in terms of the effect of Ti vacancies on mass transport in TiO_2 .

Postulation of the problem

In former studies by the authors [10], the self-diffusion coefficient of Nb, $D_{^{93}\text{Nb}}$, in undoped TiO_2 was determined to exhibit the following temperature dependence:

$$D_{^{93}\text{Nb}} = (4.7 \text{ m}^2 \text{ s}^{-1}) \times 10^{-7} \exp\left(\frac{-244 \pm 9 \text{ kJ mol}^{-1}}{RT}\right). \quad (1)$$

Whilst the determined activation energy specifically describes the temperature dependence, it is the energetic barriers related to the formation of specific defects, as well as their migration, which are controlling the diffusion of ^{93}Nb . According to Mrowec [11], the activation energy, E_a , can be described by the summation of formation and migration enthalpies:

$$E_a = \frac{2}{z} \Delta H_f + \Delta H_m \quad (2)$$

where ΔH_f is the formation enthalpy of the related defect and ΔH_m is the migration enthalpy of the diffusing species. The term z is the ionisation degree of the defects involved in transport.

In the present study, the temperature dependence of the self-diffusion of ^{93}Nb in Nb-doped TiO_2 will be determined under identical conditions of temperature and oxygen activity to those reported previously for the self-diffusion of ^{93}Nb in undoped TiO_2 [10]. In both cases, the diffusion of defects, such as extrinsic defects, is investigated, and so ΔH_f and ΔH_m correspond, respectively, to the formation and migration enthalpies of titanium vacancies. The composition of the present specimen has been altered through donor doping and subsequent high-temperature

oxidation. Such doping of TiO_2 results in an increase of the concentration of titanium vacancies [8]. Consequently, the effect of altered titanium vacancy concentration on ΔH_f and ΔH_m may be considered in a well-defined manner.

Brief literature overview

The diffusion of various cations in TiO_2 has been reported in the literature [10–20]. In particular, the self-diffusion of Ti tracer (^{44}Ti) has received substantial attention due to its relevance in the establishment of defect disorder models in TiO_2 [12–15]. Consequently, these reports have been undertaken over a broad range of temperature and oxygen activity, and according to Hoshino et al. [13], the self-diffusion of ^{44}Ti proceeds according to the interstitialcy mechanism.

A comprehensive assessment of impurity cation (^{46}Sc , ^{51}Cr , ^{54}Mn , ^{59}Fe , ^{60}Co , ^{63}Ni and ^{95}Zr) diffusion has been made by Sasaki et al. [16] and Peterson and Sasaki [17] as a function of crystal orientation, temperature, oxygen activity and Al impurity content. Impurity diffusion was concluded to proceed predominantly via the interstitialcy mechanism, in similarity to ^{44}Ti self-diffusion, except for divalent cations which exhibited extremely strong anisotropy indicating an interstitial mechanism. Diffusion studies of small, monovalent elements, such as lithium, have also exhibited such strongly anisotropic diffusion behaviour [18]. Recently, the present authors [10] reported the self-diffusion of ^{93}Nb in single crystal rutile in high oxygen activity [$p(\text{O}_2)=21$ kPa]. The bulk diffusion of ^{93}Nb was observed to compare closely to the self-diffusion of ^{44}Ti and was concluded to also diffuse via the interstitialcy mechanism.

At elevated temperatures and high oxygen activity [$p(\text{O}_2)$ in the vicinity of 21 kPa], the incorporation of a donor, such as Nb, is compensated by titanium vacancies according to the following equilibria [21, 22] (using the Kröger–Vink notation [23]) and charge neutrality condition [22]:



$$[\text{Nb}_{\text{Ti}}^{\bullet}] = 4[\text{V}_{\text{Ti}}^{\prime\prime\prime}]. \quad (4)$$

Under the experimental conditions applied in this investigation, a considerable concentration (~ 1 at.%) of cation vacancies will exist within the titanium sub-lattice, which can be expected to have a significant affect on both the rate of cation self-diffusion and the activation energy. Since previous diffusion studies [16, 17] of doped systems have involved small quantities (parts per million levels) of acceptor-type dopants, the present work reports behaviour not previously observed in TiO_2 .

Basic equations

According to Crank [24], the solution of Fick's second law for the condition of a 'plane source' is:

$$C(x, t) = \frac{M}{(\pi Dt)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (5)$$

where $C(x, t)$ is the concentration of solute at a specific distance from the specimen's surface and time, M is the surface concentration of solute at $t=0$, x is the diffusion distance, t is the diffusion time and D is the diffusion coefficient, which, in the present case, is equivalent to the self-diffusion coefficient, D_{self} . From a plot of $\log C(x, t)$ versus x^2 , D_{self} can be determined from the relation:

$$D_{\text{self}} = -\frac{1}{\text{slope} \times 2.303 \times 4t} \quad (6)$$

where slope is the gradient of the linear region of the $\log C(x, t)$ versus x^2 plot, which is predominated by self-diffusion.

As a thermally activated process, D_{self} demonstrates an Arrhenius temperature dependence:

$$D_{\text{self}} = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

where D_0 is a pre-exponential factor, R is the ideal gas constant and T is temperature. During the analysis of a diffusion experiment, E_a can be simply determined from a plot of $\log D$ versus $1/T$ and the following relation:

$$E_a = -2.303 \times m \times R \quad (8)$$

where m is the gradient of the resulting plot and R is the ideal gas constant. For a detailed discussion concerning the physical and theoretical background to diffusion, consult the texts of Mrowec [11] and Kofstad [25].

Experimental

Preparation and surface processing

The specimens were cut from a randomly oriented boule of high purity, 4.3 at.% Nb-doped single crystal TiO_2 grown by the Verneuil method (rutile; SurfaceNet, Holland) using a diamond saw such that diffusion proceeded in the same direction for each specimen. One side of each specimen was polished to a high mirror finish, after which each specimen was ultrasonically cleaned in acetone. In order to establish equilibrium defect disorder prior to the diffusion anneal, each specimen was individually pre-annealed in air [$p(\text{O}_2)=21$ kPa] at the planned diffusion temperature for time periods that greatly exceeded the planned diffusion time, as summarised in Table 1.

Table 1 Pre-annealing and diffusion annealing temperatures and times (performed in air)

Specimen	Temperature (K)	Pre-anneal time (h)	Diffusion anneal time (min)
1	1,073	96	1,440
2	1,173	72	300
3	1,373	36	15
4	1,573	24	10

Nb was deposited onto the surface of each of these specimens using a 0.125-mol/L Nb salt solution prepared from 1.69 g of NbCl_5 (Sigma Aldrich), 50 mL of ethanol (reagent grade) and five drops of HCl (reagent grade—added to the salt solution to assist the dissolution of NbCl_5). Several drops of this solution were placed on the surface of the specimen which was gently heated at 50 °C until the drops had fully dried. The Nb diffusion profiles were then imposed during annealing in air at 1,073–1,573 K for times ranging from 10 min to 24 h.

Determination of diffusion concentration profiles

The diffusion concentration profile was determined using secondary ion mass spectrometry (SIMS; Cameca IMS 5f). A Cs^+ primary ion beam of 10 kV accelerating voltage and ~75 nA primary beam current was used to sputter the surface of the specimen over a rastered area of $250 \times 250 \mu\text{m}$. In order to reduce/eliminate the likelihood of charging (due to the insulating properties of the specimen), a thin (~20 nm) gold coating was sputter deposited onto the surface of the specimens prior to analysis. As well as performing analysis for elements of interest, such as Nb, Ti, Cs, O and Au, impurity analysis was also performed, specifically addressing Al, Si, Fe and Ca, which were observed to be at background levels of detection. The sputter rate was estimated from the depth of the sputter crater to be 0.51 nm/s, determined using profilometry (Mitutoyo-Surftest SV 600).

Results

When using intensity data obtained by SIMS, it has been shown that the concentration of a species of interest can be approximated by the normalisation of this species against a stable lattice element [10]. In this manner, the normalisation of the intensity of ^{93}Nb against the intensity of ^{48}Ti can estimate the Nb concentration as shown in the following relation:

$$C_{\text{Nb}} = \frac{I(^{93}\text{Nb})}{I(^{48}\text{Ti})} \quad (9)$$

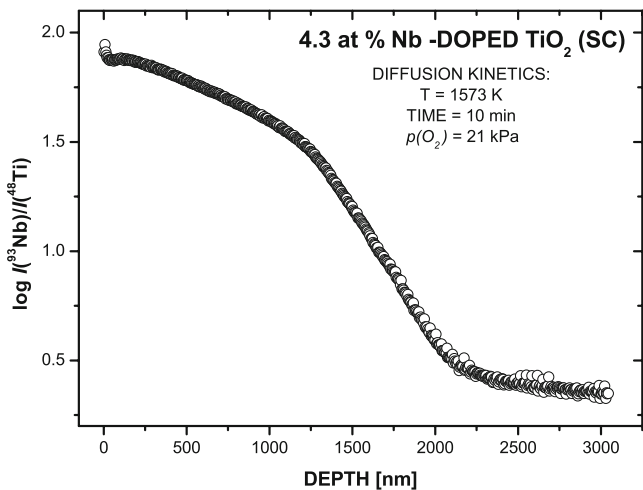


Fig. 1 ⁹³Nb diffusion profile as a function of depth into the specimen

where C_{Nb} is the concentration of Nb and $I(^{93}\text{Nb})$ and $I(^{48}\text{Ti})$ are the measured intensities obtained during SIMS analysis. Using the determined sputtering rate, the depth profile obtained for the specimen annealed at 1,573 K for 10 min is displayed in Fig. 1 (note that the kink at the beginning of the depth profile is associated with the establishment of steady-state sputtering conditions).

According to Eq. 5, it is possible to determine the self-diffusion coefficient from a plot of the logarithm of ⁹³Nb concentration versus the square of depth into the specimen's surface. This plot has been made and is displayed as Fig. 2 for the specimen annealed at 1,573 K for 10 min. It is clear in this figure that a regime described by parabolic kinetics exists, in confirmation of Eq. 5. This regime has been identified as the 'self-diffusion regime'. For improved clarity, this region is exclusively considered in Fig. 3. As indicated in this figure, the self-diffusion coefficient for ⁹³Nb under the given processing conditions can be reliably determined from the observed diffusion gradient and Eq. 6.

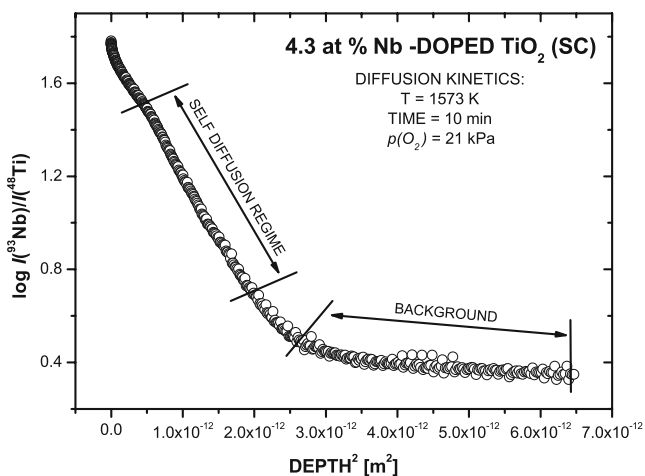


Fig. 2 ⁹³Nb diffusion profile as a function of the square of the depth

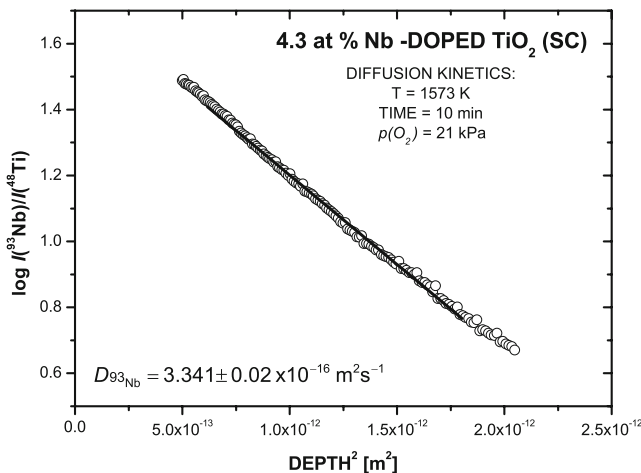


Fig. 3 Determination of ⁹³Nb self-diffusion coefficient from ⁹³Nb diffusion profile as a function of the square of the depth

In this fashion, the ⁹³Nb self-diffusion coefficient was determined under different annealing temperatures and has been plotted in an Arrhenius fashion in Fig. 4. Using Eq. 7, the activation energy has been determined to be 197±9 kJ mol⁻¹ with an overall temperature dependence described by:

$$D_{93\text{Nb}} = 1.77 \pm 7.28 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \exp\left(\frac{-197 \pm 9 \text{ kJ mol}^{-1}}{RT}\right) \quad (10)$$

Discussion

Figure 5 summarises some results reported in the literature for ⁴⁴Ti and ⁹³Nb diffusion in undoped TiO₂ along with the

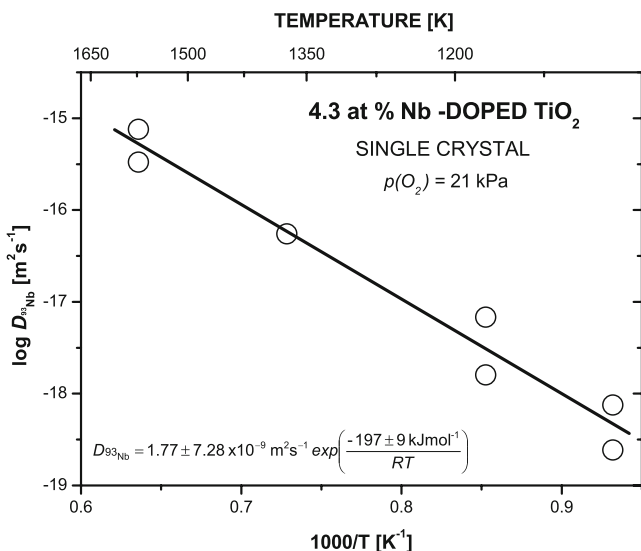


Fig. 4 Arrhenius dependence of ⁹³Nb self-diffusion in Nb-doped TiO₂ single crystal

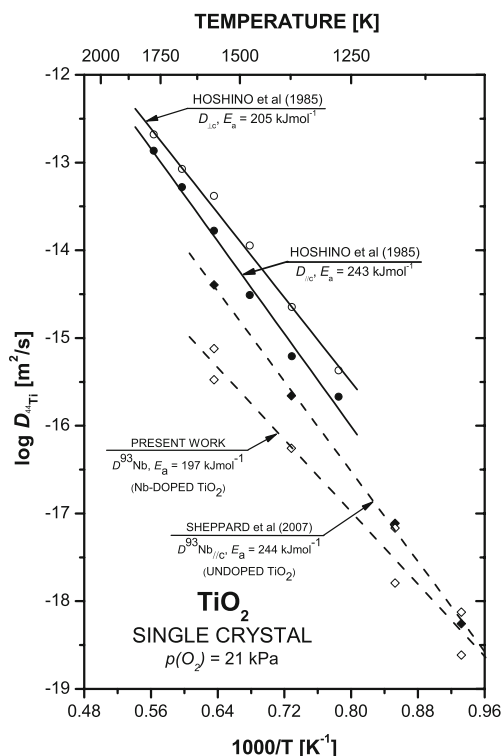


Fig. 5 Comparison of presently obtained ^{93}Nb self-diffusion coefficients to relevant literature results

presently obtained result for ^{93}Nb self-diffusion in Nb-doped TiO_2 [10, 13]. As seen, the present result varies substantially from these literature reports in respect to both the activation energy and the magnitude of the diffusion coefficient. The observed behaviour of the self-diffusion of ^{93}Nb in the present study is noticeably slower than that observed for the ^{93}Nb tracer diffusion in undoped TiO_2 [10], indicating a clear effect of altered bulk composition.

The interstitialcy mechanism has been proposed for the self-diffusion of ^{44}Ti in undoped TiO_2 [13]. Based on the similarity of behaviour when compared to ^{44}Ti , the interstitialcy mechanism has also been proposed for the tracer diffusion of ^{93}Nb in undoped TiO_2 [10]. This mechanism involves the coordinated migration of cations from interstitial to regular lattice sites, and therefore, should be promoted by an increase in the concentration of titanium vacancies. In the present case, the titanium vacancy concentration has been increased via donor

doping. However, this has failed to increase the rate of self-diffusion.

It is difficult to provide a reasonable explanation for this effect, and the possibilities are highly speculative, such as a change in the diffusion mechanism or a dramatic decrease in the jump frequency [11]. Further analysis and experimentation is required, but outside the scope of this single paper. Nonetheless, it is clear that the rate of ^{93}Nb self-diffusion is related to the amount of ^{93}Nb in the host lattice. Therefore, during doping, one can expect that the self-diffusion coefficient may alter during the time of incorporation, especially when the dopant concentration is high.

An activation energy, E_a , of 197 kJ mol^{-1} has been determined in the present study. When compared to the activation energy of 244 kJ mol^{-1} reported for ^{93}Nb tracer diffusion in undoped TiO_2 , it is clear that doping has had a significant affect on the energetic parameters related to diffusion. As shown by Eq. 2, the activation energy is related to the summation of formation and migration enthalpies for specifically involved defects. In the present case, the self-diffusion of ^{93}Nb is assumed to proceed according to the availability of titanium vacancies. Hence, Eq. 2 is slightly modified to reflect these defects:

$$E_a = \frac{1}{2}\Delta H_f(V_{\text{Ti}}) + \Delta H_m(V_{\text{Ti}}) \tag{11}$$

where $\Delta H_f(V_{\text{Ti}})$ and $\Delta H_m(V_{\text{Ti}})$ are, respectively, the formation and migration enthalpies for a titanium vacancy. The term, z , is equal to 4, as titanium vacancies will be fully ionised in the presently studied temperature range.

Literature data relating to $\Delta H_f(V_{\text{Ti}})$ and $\Delta H_m(V_{\text{Ti}})$ is scarce. The only value available for $\Delta H_f(V_{\text{Ti}})$ is 224 kJ mol^{-1} reported by Hossain et al. [26]. This is based upon ab initio calculation for a titanium vacancy in an undoped TiO_2 lattice. The only value available for $\Delta H_m(V_{\text{Ti}})$ is 134 kJ mol^{-1} reported by Nowotny et al. [27] which was determined experimentally from chemical diffusion data obtained during the prolonged oxidation of undoped TiO_2 single crystal. Employing these values and Eq. 11 yields a hypothetical activation energy of 246 kJ mol^{-1} . This is remarkably close to the activation energy reported for ^{93}Nb tracer diffusion in undoped TiO_2 ($E_a = 244 \text{ kJ mol}^{-1}$) which provides confirmation for the role of titanium vacancies in the diffusion mechanism. However, it is clear that, for the present investigation ($E_a = 197 \text{ kJ mol}^{-1}$), $\Delta H_f(V_{\text{Ti}})$,

Table 2 Summary of calculated and assumed enthalpy values

	$\Delta H_m(V_{\text{Ti}})$ (kJ mol^{-1})	$\Delta H_f(V_{\text{Ti}})$ (kJ mol^{-1})	E_a (kJ mol^{-1})
Literature enthalpy values for undoped TiO_2	134 [25]	224 [24]	246 (calculated)
^{93}Nb -doped TiO_2 $\Delta H_m(V_{\text{Ti}})$ assumed constant	134 (assumed)	126 (calculated)	197 (determined)
^{93}Nb -doped TiO_2 $\Delta H_f(V_{\text{Ti}})$ assumed constant	85 (calculated)	224 (assumed)	197 (determined)
^{93}Nb -doped TiO_2 $\Delta H_m(V_{\text{Ti}})$ and $\Delta H_f(V_{\text{Ti}})$ not constant	85–134	126–224	197–246

$\Delta H_m(V_{Ti})$ or both, vary significantly from the undoped TiO_2 case due to the altered bulk composition resulting from doping.

Several scenarios can be proposed for determining values for $\Delta H_f(V_{Ti})$ and $\Delta H_m(V_{Ti})$ in Nb-doped TiO_2 from the presently determined activation energy for ^{93}Nb self-diffusion. Firstly, it may be assumed that $\Delta H_m(V_{Ti})$ is independent of changes in composition (at least over the presently considered range), and therefore, is equal to 134 kJ mol^{-1} based on the undoped case [27]. Using this value for $\Delta H_m(V_{Ti})$, E_a equal to 197 kJ mol^{-1} , solving Eq. 11 for $\Delta H_f(V_{Ti})$ yields 126 kJ mol^{-1} . This is substantially less than the $\Delta H_f(V_{Ti})$ value reported by Hossain et al. [26] for undoped TiO_2 , but may be legitimate due to the compositional change.

Alternatively, it could also be assumed that $\Delta H_f(V_{Ti})$ is independent of compositional changes over the considered range. In this case, Eq. 11 may be solved for $\Delta H_m(V_{Ti})$ using the $\Delta H_f(V_{Ti})$ value of 224 kJ mol^{-1} reported by Hossain et al. [26] and the same value for E_a as previously employed. In this case, $\Delta H_m(V_{Ti})$ is calculated to be 85 kJ mol^{-1} which is also substantially less than the value of 134 kJ mol^{-1} reported for $\Delta H_m(V_{Ti})$ for undoped TiO_2 . Yet this value is consistent with the reported activation energy for chemical diffusion (88 kJ mol^{-1} —equivalent to ΔH_m) determined for 0.65 at.% Nb-doped TiO_2 under similar experimental conditions [28]. However, it remains unclear whether this value truly relates to the migration of titanium vacancies or is instead related to the migration of oxygen vacancies which have been observed in undoped TiO_2 to equilibrate much faster than titanium vacancies. Nonetheless, a reduction in strain energy, and correspondingly, $\Delta H_m(V_{Ti})$, could be expected due to the increased presence of cation vacancies in the lattice as a result of donor doping.

The third possible scenario which can be proposed is one in which both $\Delta H_m(V_{Ti})$ and $\Delta H_f(V_{Ti})$ are significantly affected by changes in specimen composition. Given the limited availability of data, this possibility cannot be addressed. However, it can be concluded that the values used and calculated in the previous two scenarios provide the extreme boundaries for $\Delta H_m(V_{Ti})$ and $\Delta H_f(V_{Ti})$ under the present experimental conditions. Therefore, $85 \text{ kJ mol}^{-1} < \Delta H_m(V_{Ti}) < 134 \text{ kJ mol}^{-1}$ and $126 \text{ kJ mol}^{-1} < \Delta H_f(V_{Ti}) < 224 \text{ kJ mol}^{-1}$ for ^{93}Nb self-diffusion in ^{93}Nb -doped TiO_2 . For summary purposes, these different values and scenarios have been collated in Table 2.

Conclusions

The present project has determined the temperature dependence of ^{93}Nb self-diffusion in 4.3 at.% Nb-doped TiO_2 single crystal at high oxygen activity [$p(O_2)=21 \text{ kPa}$]. The

activation energy for diffusion has been determined to be 197 kJ mol^{-1} . This value differs significantly from the reported value for ^{93}Nb tracer diffusion in undoped TiO_2 , indicating the effect of altered composition. Considering this effect in terms of defect migration and formation enthalpies, it appears that the migration enthalpy of a titanium vacancy may be more sensitive to compositional change than the formation enthalpy. However, this conclusion is based on assumptions and requires further confirmation. Nonetheless, the migration and formation enthalpies of titanium vacancies can safely be considered to, respectively, span 85–134 and 126–224 kJ mol^{-1} in Nb-doped TiO_2 for Nb doping up to ~4 at.%. The rate of ^{93}Nb self-diffusion in Nb-doped TiO_2 was observed to be slower than in undoped TiO_2 which also indicates a significant compositional effect. It is very clear from the present investigation that diffusion behaviour varies as the bulk composition is altered. In particular, the rate of ^{93}Nb incorporation depends upon the amount of ^{93}Nb already incorporated. This has immediate practical consequence during doping where self-diffusion is unavoidably relied upon to induce a predictable compositional change in the intended specimen.

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