Protons in acceptor doped langasite, La₃Ga₅SiO₁₄

Tor Svendsen Bjørheim, Reidar Haugsrud, Truls Norby*

Centre for Materials Science and Nanotechnology. Department of Chemistry, University of Oslo, FERMIO, Gaustadalleen 21, NO-0349 Oslo, Norway

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The electrical and defect chemical properties of acceptor doped langasite have been investigated over wide ranges of pH₂O, pO₂ and temperature. All compositions are pure proton conductors up to 800 °C in wet atmospheres and mixed oxide ion-p-type conductors at higher temperatures. The enthalpy of mobility of protons is 75 ± 3 kJ/mol, while that of oxygen vacancies is 125 ± 7 kJ/mol. The standard enthalpy and entropy of hydration ranges of pH₂O,pO₂ and temperature. All compositions are pure proton conductors up to 800 °C in wet atmospheres and mixed oxide ion-p-type conductors at higher temperatures. The enthalpy of mobility of protons is 75 ± 3 kJ/mol, while that of oxygen vacancies is 125 ± 7 kJ/mol. The standard enthalpy and entropy of hydration are -100 ± 3 kJ/mol and -157 ± 5 J/mol K, respectively. Langasite based sensors may therefore be affected by dissolution of protons from H₂O in the bulk crystal lattice up to temperatures as high as 1000 °C.

1. Introduction

Lanthanum gallium silicate, La₃Ga₅SiO₁₄, or langasite, has attracted considerable attention in the last decade, mainly due to its piezoelectric properties, and finds application in bulk acoustic wave (BAW) and surface acoustic wave (SAW) devices. Unlike traditional piezoelectrics such as quartz, LiNbO₃ or Pb(Zr,Ti)O₃ (PZT), langasite displays no phase transitions and retains its piezoelectric properties up to the melting point at 1470 °C [1]. Further, high quality single crystals are readily available through the conventional Czochralski technique [2]. Traditional quartz crystal microbalances (QCMs) are usually operated at, or close to, room temperature. Langasite based BAW devices have on the other hand been successfully operated up to 1400 °C [3], making langasite particularly interesting for use in high temperature microbalances and gas sensors.

The langasite family of oxides takes on a trigonal structure with symmetry P2₁ (space group 32) and is isostructural with Ca₃Ga₅Ge₄O₁₄ [2,4]. The structure, with general formula A₃BC₃D₂O₁₄ encompasses 4 distinct cation sites, where A is coordinated to 8 O ions, B is 6 coordinated (octahedral), while C and D are 4 coordinated (tetrahedral and planar trigonal pyramidal coordinations, respectively). In langasite, La occupies the A site, Ga the B, C and half of the D sites, while Si only occupies the D sites (Fig. 1). The structure allows for large compositional variations, and there exists over 100 multicomponent oxides within the langasite family [2]. The most widely studied langasite type oxides are La₃Ga₅Ta₃O₁₄ (langatate) [5,6] and La₃Ga₅Nb₃O₁₄ (langanite) [7], in addition to langasite itself. Compositions with complete substitution of Si by Ge, Sn and Ti have also been successfully grown as single crystals. Similarly, RE₃Ga₅SiO₁₄ (RE = Pr, Nd) takes on the langasite structure [8–10], while the smaller rare-earth ions are unstable with respect to garnet formation (RE₃Ga₅O₁₂) [11]. Due to partial cation disorder, the langasite type oxides are prone to variations in the ratio of B, C and D site elements, and for langasite variations in the Ga/Si ratio result in intrinsic acceptor/donor doping.

In terms of electromechanical properties, the most widely studied oxide within the langasite family is langasite itself. Seh and Tuller [12, 13] have investigated the defect chemistry and transport properties of acceptor (1% of La substituted by Sr) and donor (5% of Ga substituted by Nb) doped polycrystalline langasite in the temperature and pO₂ range of 700 to 1000 °C and 10⁻²⁵ to 1 atm, respectively. The conductivity of undoped langasite was pO₂ independent under oxidizing conditions and proportional to pO₂¹/₄ under more reducing conditions, reflecting oxide ion and n-type electronic conductivity, respectively. For 1% Sr doped langasite, the n-type conductivity was completely suppressed, resulting in pure oxide ion conductivity over a large pO₂ and temperature range, and a minor contribution from electron holes at the highest temperatures. The activation energy of ionic conductivity was found to be higher in acceptor doped (123 ± 2 kJ/mol) than nominally undoped langasite (88 ± 2 kJ/mol) [5], 5% donor doped (Nb doped) langasite on the other hand displayed a pO₂¹/₆ dependent conductivity under reducing conditions, and pO₂ independent conductivity under oxidizing conditions. Electrons and oxygen vacancies were suggested to dominate concentration-wise under reducing conditions, while ionized Nb donors and electrons dominate under more oxidizing conditions. Electrons were further proposed as the dominating charge carrier over the entire pO₂ and temperature range.

The electrical and defect chemical properties of acceptor doped langasite have been investigated over wide ranges of pH₂O, pO₂ and temperature. All compositions are pure proton conductors up to 800 °C in wet atmospheres and mixed oxide ion-p-type conductors at higher temperatures. The enthalpy of mobility of protons is 75 ± 3 kJ/mol, while that of oxygen vacancies is 125 ± 7 kJ/mol. The standard enthalpy and entropy of hydration are -100 ± 3 kJ/mol and -157 ± 5 J/mol K, respectively. Langasite based sensors may therefore be affected by dissolution of protons from H₂O in the bulk crystal lattice up to temperatures as high as 1000 °C.

* Corresponding author.
E-mail address: truls.norby@kjemi.uio.no (T. Norby).
Langasite unit cell with Ga in green (B, C and half of the D sites), and Si in blue polyhedral (half of the D sites), and La ions (A) as yellow spheres. Ga and Si randomly occupy the D site. O1 ions are shown in black, O2 in blue and O3 in red.

Fig. 1. Langasite unit cell with Ga in green (B, C and half of the D sites) and Si in blue polyhedral (half of the D sites), and La ions (A) as yellow spheres. Ga and Si randomly occupy the D site. O1 ions are shown in black, O2 in blue and O3 in red.

Langasite are characterized over a broad $p_{\text{H}_2\text{O}}$, $p_{\text{O}_2}$, and temperature range using AC impedance spectroscopy. The water uptake is determined using thermogravimetric measurements. In addition to the experimental approaches, first principles density functional theory calculations are employed to evaluate the importance of various potentially dominating charge-compensating defects, notably OH\text{-}, O\text{\textit{H}}\text{-}, O\text{\textit{H}}\text{\textsuperscript{3}\text{-}}, and H\text{\textit{i}}, in acceptor or donor doped langasite.

2. Computational procedures

2.1. Computational setup

All first principles calculations were performed using the density functional theory approximation as implemented in the VASP software [17–20]. Exchange and correlation were treated by the generalized gradient approximation functional due to Perdew, Burke and Ernzerhof [21] and the projector augmented-wave (PAW) method [22] with a constant plane-wave cut-off energy of 500 eV. Calculations on defect free systems were performed by relaxing all ionic positions, lattice volumes and shape, while for all defect calculations, the volumes of the defective cells were fixed to those of the defect free bulk cells. Electronic relaxation was performed to within an energy difference of $10^{-6}$ eV for self-consistency, while ionic optimizations were performed until all residual forces were smaller than 0.02 eV/Å.

2.2. Defect structure from first principles

Defect formation energies were evaluated by:

$$\Delta G_{\text{defect}}^f = E_{\text{tot}}^{\text{defect}} - E_{\text{tot}}^{\text{bulk}} + \sum_i \Delta \mu_i q (\mu_e + \Delta \epsilon)$$

where $\Delta \mu_i$ is the change in the number of atom i with chemical potential $\mu_e$, $q$ is the effective charge of the defect, $\mu_e$ is the Fermi level and $\Delta \epsilon$ aligns the core potentials of the perfect and the defective supercells to remedy shifts in the band edges due to the jellium background charge. Finite temperature and partial pressure defect formation energies were estimated from the temperature dependencies of $\mu_e$:

$$\mu_e(T, p_i) = \mu_e^0 + H_1^1(T) - TS_1(T) + k_B T \ln \left( \frac{P_i}{P} \right)$$

where $\mu_e^0$ is determined by the total energy of the pure phases at 0 K as obtained from DFT, whereas the second and third terms are set equal to tabulated values [23]. To avoid the large uncertainty arising from overbinding of the O\text{-} molecule, we obtain $\mu_e^0$ by assuming the equilibrium gas mixture H\text{\textit{2}}O(g) + H\text{\textit{2}}(g) in which $\mu_e$ is given by $\mu_e^0 = p_{\text{H}_2\text{O}} - 2 p_{\text{H}_2}$.

Finite temperature and partial pressure defect formation concentrations were obtained through:

$$C_i = N_c i \exp \left( - \frac{\Delta G_{\text{defect}}^f}{k_B T} \right)$$

where $C_i$ is the number of regular positions per unit volume (e.g., concentration of oxygen ions) and $N_c$ is the number of configurations the defect may attain at each position. Finally, the defect concentrations at lattice site s are limited to saturation of the site:

$$\sum_i^n C_i + c_{s,i} = c_{s,0}$$

where $C_i$ is the number of distinct defects formed at each site while $c_{s,i}$ is the number of lattice sites per unit volume.
The Fermi level is determined by the weighted concentrations of all N charged defects (electroneutrality):

$$\sum_{j=1}^{N} q_j c_j = 0.$$  \hfill (6)

As the band gap is heavily underestimated in our calculations (3.6 vs. 4.1–4.9 eV [24]), we have neglected electronic defects from Eq. (6).

3. Experimental

3.1. Sample preparation

Polycrystalline langasite was acceptor doped either by Sr substitution or by increasing the Ga/Si ratio above stoichiometric 5:1. The nominal compositions La$_{2.94}$Sr$_{0.06}$Ga$_5$SiO$_{14}$ (hereafter denoted as “6Sr:LGs”) and La$_{2.001}$Ga$_{5-x}$Si$_{1+y}$O$_{14-z}$ (X = 0.06 and 0.12—hereafter denoted as “6Ga:LGs” and “12Ga:LGs”) were prepared through a solid state route with La$_2$O$_3$ (Sigma-Aldrich 99.99%), Ga$_2$O$_3$ (Alfa Aesar 99.9%), SiO$_2$ (Alfa Aesar 99.9%) and SrCO$_3$ (Sigma-Aldrich 99.9%) as starting powders. Being highly hygroscopic, La$_2$O$_3$ was dried at 900 °C prior to weighing. The powders were mixed by ball milling for 2 h prior to sintering. The powders were again milled for 1 h at 250 rpm, and cold-pressed to pellets with a diameter of 13 mm under an isostatic, uniaxial pressure of 100 MPa and finally sintered at 1400 °C for 1 h. The relative densities of the sintered 6Sr:LGs, 6Ga:LGs and 12Ga:LGs samples were 87, 85 and 89%, respectively. In addition, we have characterized the electrical properties of a Czochralski grown langasite single crystal cut normal to the y-axis (hereafter denoted “SC”) from the Institute for Crystal Growth, Berlin-Adlershof, Germany.

Circular Pt electrodes with a diameter of 1 cm were attached to both sides of the polycrystalline samples prior to measurements, while for the single crystal a 0.2 mm thick Pt wire was attached to each side of the sample using Pt ink. The electrodes were fired by annealing the samples at 1100 °C for 1 h.

The phase purity of the materials was analyzed by X-ray diffraction (XRD, Bruker D8 Discover, Cu Kα, Bragg-Brentano) and scanning electron microscopy (SEM, FEI Quanta 200F) with energy dispersive spectroscopy (EDS, EDAX Pegasus 2200) was applied to characterize the microstructure and chemical composition after sintering. A second-generation electron microscopy (SEM, FEI Quanta 200F) was applied to characterize the microstructure and chemical composition after sintering. A second-generation electron microscopy (SEM, FEI Quanta 200F) was applied to characterize the microstructure and chemical composition after sintering. A second-generation electron microscopy (SEM, FEI Quanta 200F) was applied to characterize the microstructure and chemical composition after sintering.

3.2. Electrical characterizations

AC conductivity and impedance measurements were performed in a ProboStat measurement cell (NorECs, Norway) using an HP 4192 LF impedance spectrometer. Constant AC frequency measurements were performed at 10 kHz, while impedance spectra were recorded within the frequency range from 1 MHz to 1 Hz. Specific conductivities were calculated from sample geometry, while porosity corrections were not included. The electrical properties were measured versus the partial pressure of oxygen, $p_{O_2}$, in the range $10^{-5}$–1 atm with constant water vapor partial pressure, $p_{H_2O}$ = 0.03 atm and, moreover, versus $p_{H_2O}$ in the range $3 \times 10^{-5}$–0.03 atm in oxygen.

3.3. Thermogravimetry

The water uptake of all polycrystalline samples was measured using a Netsch STA449 F1 thermogravimetric analyzer in wet Ar ($p_{H_2O}$ = 0.02 atm) within the temperature interval 1000 to 250 °C. The samples were crushed and ground thoroughly in a ball mill at 250 rpm for 1 h prior to measurements to ensure a homogeneous particle distribution. The samples were initially kept at 1000 °C for 6 h in bottle dry $O_2$, and the water uptake was measured isothermally every 50 °C from 900 to 250 °C with a cooling rate of 5 °C/min between the temperature intervals. At each temperature, the samples were let to equilibrate for 4–12 h. The weight change due to buoyancy was corrected for by subtracting the weight change of an empty crucible using an identical program.

4. Results and discussion

4.1. Defect structure from first principle calculations

In all defect calculations, we have chosen a “random” Ga/Si distribution or by increasing the Ga/Si ratio above stoichiometric 5:1. The calculated relative stability of oxygen vacancies (doubly charged) on the different oxygen sites. The O3 and O1 vacancies are equally stable on the O3 ions, which are bound to one octahedral (B site) and one tetrahedral (C site) Ga ion, and two La ions. Removal of either the O2 ions, which are coordinated to two tetrahedral Ga or Si (one C and one D site) and two La ions, or the O1 ions which are coordinated to one tetrahedral Ga or Si (D site) and 3 La, is significantly less favorable. This may be explained by the fact that removal of O1 or O2 ions breaks the smaller and more strongly bonded SiO$_4$ and GaO$_4$ units, resulting in unstable 3-fold coordinated Si and Ga on the D site.

Fig. 2 shows all unique OH$^-$ configurations within a 1 × 1 × 2 unit of langasite, with their relative stabilities in Table 2. Note that only symmetrically non-equivalent sites are shown for half of the 1 × 1 × 2 unit (except for site c to illustrate the rotational symmetry of the primitive unit). There are two stable configurations on each O2 and O3 ion close to D site Ga or Si. On O1 bound to Ga we find one stable position with a 3-fold degenerate rotational symmetry. All similar positions on O1 bound to Si relaxed either to the e1 or e2 site. The most stable proton site is the b2 site, which is bound to an O3 ion close to D site Ga, while the equivalent site close to Si, e2, is slightly less stable. Further, the sites on O1 and O2 are all higher in energy, and the sites close to Si are in general less stable than those close to Ga. As for oxygen vacancies there seemingly is an effect of coordination of the O ions on the stability.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Relative stability (in kJ/mol) of OH$^-$ on O1, O2 and O3 sites surrounding either Ga or Si on the cation D site.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ga</td>
</tr>
<tr>
<td>O1</td>
<td>168</td>
</tr>
<tr>
<td>O2</td>
<td>77</td>
</tr>
<tr>
<td>O3</td>
<td>5</td>
</tr>
</tbody>
</table>
of protons. The most stable proton sites are on the O3 ions which are bound to one octahedral and one tetrahedral Ga (B and C site) and two La ions. Protons are notably less stable on the O1 and O2 ions, which only are bound to the tetrahedrally coordinated Ga/Si (sites C and D) and La ions. Hence, both protons and vacancies are most stable in regions of the unit cell with the higher oxygen density.

For O$^{2-}$ and OH$^{-}$ interstitials, the most stable positions were all displaced slightly from the center of the La channels, and bound either to one D site Ga/Si and one C site Ga, or to two neighboring C site Ga.

4.1.2. Defect thermodynamics and defect structure

The main motivation of this study is to determine the role of protons, oxygen vacancies, oxide ion interstitial and hydroxide interstitials as dominating charge compensation defects in langasite. The formation and predominance of these defects may be addressed from the hydration reaction (Eq. (1)) and the following defect reactions:

$$\text{H}_2\text{O}(g) + \text{O}_0^\text{O} \leftrightarrow \text{OH}_0^\text{O} + \text{OH}_1^\text{hi}$$  \hspace{1cm} (7)

$$\text{H}_2\text{O}(g) + 2\text{O}_0^\text{O} \leftrightarrow 2\text{OH}_0^\text{O} + \text{O}_1^\text{hi}$$  \hspace{1cm} (8)

$$\text{O}_0^\text{O} \leftrightarrow \text{V}_0^\text{O} + \text{O}_1^\text{hi}.$$  \hspace{1cm} (9)

Based on the defect formation energies determined by DFT calculations, the enthalpies of Eqs. (1) and (7)–(9) are $-106$, $105$, $154$ and $270$ kJ/mol, respectively. Hence, acceptor doped langasite will hydrate oxygen vacancies according to Eq. (1), while the contributions to the defect structure from the reactions in Eqs. (7)–(9) are small.

The high temperature defect structure of langasite may be estimated from the defect formation energies at finite temperatures (Eqs. (2) and (3)) with Eqs. (4)–(6). The reader should note that, although phonon contributions to the defect formation entropies are neglected, the approach gives a qualitative picture of the material’s defect chemistry. Fig. 3 presents the concentration of OH$^\text{O}$, OH$^\text{i}$, O$^\text{O}$ and H$^\text{i}$ at 800 K in 3% wetted O$_2$ as a function of the concentration of frozen-in donors (left panel) and acceptors (right panel) obtained from the DFT calculations. Intrinsic langasite (i.e., with donor/acceptor concentrations below the ppm range) is expected to be dominated by anti-Frenkel disorder (Eq. (9)) under dry conditions, and oxide ion interstitials and protons under wet conditions (Eq. (8)).

$$2\text{V}_0^\text{O} + [\text{OH}_0^\text{O}] = 2\text{O}_1^\text{hi}.$$  \hspace{1cm} (10)

The defect concentrations in this intrinsic region are, however, small, and will be overshadowed by small amounts of impurities or off-sets in the Ga/Si ratio. In the acceptor doped regime, oxygen vacancies and protons charge-compensate the acceptor:

$$2\text{V}_0^\text{O} + [\text{OH}_0^\text{O}] = [\text{A}^\text{hi}].$$  \hspace{1cm} (11)

and langasite here hydrates by dissolution of protons at the expense of oxygen vacancies, according to Eq. (1). In the donor doped regime, the calculations predict oxide ion interstitials as the dominating charge-compensating defect:

$$[\text{D}^\text{hi}] = 2\text{O}_1^\text{hi}.$$  \hspace{1cm} (12)

Seh and Tuller [13] suggested Nb doped langasite to be dominated by electrons and ionized donors even under oxidizing conditions, i.e. that formation of oxide ion interstitials is considerably less favorable than formation of electronic defects. In our calculations, however, the equilibrium Fermi level is found at mid-gap values for all donor concentrations, indicating small concentrations of electronic defects under oxidizing conditions. Although our calculations are prone to underestimated defect formation entropies and the band gap (which affects the electron concentration), these results may also indicate that the p$_\text{O}_2$ independent conductivity reported by Seh and Tuller [13] reflects the situation in Eq. (12) and thus a dominating oxide ion interstitial conductivity.

For all donor/acceptor concentrations, the concentration of OH$^\text{O}$ is small. Although the defect formation entropy is uncertain, we expect

![Fig. 2](attachment:image2.png)

**Fig. 2.** All unique proton positions within a $1 \times 1 \times 2$ unit of langasite. O1 ions are shown in black, O2 in blue and O3 in red. The 3-fold degenerate symmetry equivalent c sites are shown to illustrate the rotational symmetry of the primitive unit. The corresponding relative energies are shown in Table 1.

![Fig. 3](attachment:image3.png)

**Fig. 3.** Equilibrium concentration of selected defects as a function of donor and acceptor concentration in langasite at 800 K, p$_\text{O}_2$ = 0.03 atm and p$_\text{O}_0$ = 1 atm.

<table>
<thead>
<tr>
<th>Ga</th>
<th>Si</th>
</tr>
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<tbody>
<tr>
<td>a1</td>
<td>26</td>
</tr>
<tr>
<td>a2</td>
<td>61</td>
</tr>
<tr>
<td>b1</td>
<td>12</td>
</tr>
<tr>
<td>b2</td>
<td>0</td>
</tr>
<tr>
<td>c</td>
<td>37</td>
</tr>
</tbody>
</table>

**Table 2**

Relative stability of OH$_0$ on O1, O2 and O3 sites surrounding either Ga or Si on the cation D site. All numbers are in kJ/mol and the labels refer to those used in Fig. 2.
the dominating electroneutrality in Eq. (11). The defect formation energies are obtained from DFT calculations while entropies are taken as tabulated gas phase entropies.

Concentration of \( vO \) would, however, increase rapidly with decreasing \( pO_2 \), and we do not disregard the possibility of hydride ions contributing to the properties of langasite under very reducing conditions.

Our experiments are carried out on acceptor doped langasite in which \( OH_2^+ \) and \( vO \) dominate the defect structure. The population of the different \( OH_2^+ \) and \( vO \) configurations in such a system may be evaluated from the calculated relative energies (see Fig. 4). We note that the concentration of \( vO \) on the O3 sites far exceeds the concentration of \( vO \) on any of the O1 and O2 sites within the experimental temperature interval. The concentration of \( OH_2^+ \) species is also highest on the O3 sites, in particular the b2 site. However, the concentration ratio decreases with increasing temperature, and also the e1/e2 and b1 sites will be populated by \( OH_2^+ \) to some extent at the highest temperatures.

4.2. Electrical characterizations

Fig. 5 shows impedance spectra of the polycrystalline langasite samples at 600 °C in wet \( O_2 \). The spectra exhibit 2–3 impedance contributions, depending on temperature and sample composition, and were therefore curve fitted to the equivalent circuit \( (R_1C_1)(R_2C_2)(R_3C_3) \), after subtraction of the parallel stray capacitance. The three contributions were attributed to bulk, \( R_b \), grain boundaries, \( R_g \), and an electrode response, \( R_3 \). The bulk capacitances reflect a relative permittivity of 20–100, depending on temperature and composition, which is in good agreement with literature values for langasite [14]. Further, since the 10 kHz data point mainly reflects the bulk response, all isobaric measurements on the polycrystals are performed using this frequency and a constant cooling rate of 12 °C/h. Isothermal measurements at selected temperatures after thermal equilibration of the samples showed that the isobaric measurements of the polycrystals reflect the equilibrium situation. For the single crystal, the isobaric measurements were, however, found to deviate from the isothermal measurements at lower temperatures, and all measurements were therefore performed after equilibrating the sample at each temperature/atmospheric condition.

Fig. 6 shows the bulk conductivity of the four compositions as a function of inverse temperature, measured in \( H_2O \) and \( D_2O \) wetted \( O_2 \) and \( Ar \), and dry \( O_2 \). The conductivity generally increases with increasing temperature and, interestingly, with increasing \( pH_2O \). The effect of water vapor is minute at the highest temperatures, but becomes more pronounced at lower temperature. Further, there is a notable isotope effect on the conductivity of all samples below 800 °C, which increases with decreasing temperature. Hence, protons do not only dissolve in langasite, but also dominate the bulk conductivity of all compositions below 800 °C.

Fig. 7 shows the bulk conductivity of \( 6Ga:LGS \) and \( 12Ga:LGS \) as a function of inverse temperature in wet \( O_2 \) and \( Ar \). The conductivity is close to \( pH_2O \) independent at lower temperatures. Above 700 °C, however, the conductivity decreases with decreasing \( pH_2O \), and the effect increases with increasing temperature, indicative of a minor contribution from electronic defects to the bulk conductivity. The magnitude of the \( pH_2O \) dependency of the conductivity is slightly higher for \( 6Ga:LGS \) than for \( 12Ga:LGS \), while the temperature on-set of the effect is higher for the latter, as expected from the change in the concentration ratio of doubly charged oxygen vacancies and singly charged electron holes with increasing doping level. The \( pH_2O \) dependency of the conductivity for \( SC \) and \( 6Sr:LGS \) was only measured isothermally at 1000, 900 and 800 °C (not shown) and were qualitatively similar to those of \( 6Ga:LGS \) and \( 12Ga:LGS \). Hence, in the present \( pH_2O \) window (-1 × 10⁻⁵ to -1 atm \( O_2 \)) the conductivity of all compositions is, depending on temperature and water vapor pressure, dominated by oxygen vacancies/ions and protons both concentration- and conductivity-wise. Even at the highest temperatures, there is only a small contribution from minority electron holes to the bulk conductivity, in line with the findings of Seh and Tuller [12].

Fig. 8 displays the bulk conductivity as a function of \( pH_2O \) in oxygen from 1000 to 600 °C for the single crystal and the two Ga doped polycrystals (\( 6Ga:LGS \) and \( 12Ga:LGS \)). As evident from the isobaric measurements (Fig. 6), the conductivity is essentially independent of \( pH_2O \) at 1000 °C. The \( pH_2O \) effect increases with decreasing temperature and increasing \( pH_2O \). In line with the measurements of Fritz et al. on Y-cut single crystal langasite [14]. At the lower temperatures, the effect is more pronounced for the samples with the lowest conductivities (i.e., with lower doping levels). At 600 °C, the conductivity of \( SC \) and \( 6Ga:LGS \) is close to \( pH_2O \) dependent over the entire \( pH_2O \) range, in accordance with the functional pressure dependence of pure proton conduction for hydration following Eq. (1) with:

\[
[A] = 2 [V_0^+] \quad \text{(13)}
\]

as the predominating electroneutrality. The higher doping level of \( 12Ga:LGS \) increases the concentration ratio of \( V_0^+ \) to \( OH_2^+ \) at a given

\[
\begin{align*}
\frac{[A]}{[OH_2^+]} &= 2 \\
\frac{[A]}{[OH_2^+]} &= \frac{2}{1}
\end{align*}
\]

and were, therefore, curve fitted to the equivalent circuit:

\[
(R_1C_1)(R_2C_2)(R_3C_3)
\]
temperature, resulting in smaller relative contribution from protons to the overall conductivity.

Finally, the significant isotope effect and the close to $p^{1/2}$ dependent conductivity of all compositions, support that $\text{OH}^{-}$ are the dominating protonic species (and not $\text{OH}^-$), and that $\text{O}^i$ do not act as charge-compensating defects according to Eqs. (8) and (10) (which would yield $\sigma_{\text{H}^+} \propto p^{1/3}$).

4.3. Thermogravimetric analyses

Fig. 9 shows the measured water uptake in 6Sr:LGS and 12Ga:LGS (symbols) presented as mol $\text{OH}^{-}$ per mol oxide. The solid lines represent the water uptake profiles curve fitted to Eq. (16). The water uptake clearly increases with decreasing temperature and levels off at the lowest temperatures, in line with the exothermic nature of Eq. (1). The water uptake is more pronounced for 12Ga:LGS than 6Ga:LGS, as expected from the higher nominal doping level. If interpreted similarly as for an acceptor doped oxide, the saturation level corresponds to the acceptor concentration:

$$[A^+] = [\text{OH}^-]$$

and accordingly gives an estimate of the effective acceptor concentrations, ~2 and ~5 mol% (mol/mol oxide) for 6Ga:LGS and 12Ga:LGS. For 6Sr:LGS the water uptake was lower than for 6Ga:LGS, and too low for quantification throughout larger parts of the temperature interval. However, as an estimate of the effective acceptor concentration, we use the maximum water uptake which was observed at 250 °C, corresponding to an acceptor concentration of ~1 mol%. The water uptake of the single crystal was below the detection limit throughout the entire temperature interval.

5. Discussion

5.1. Hydration thermodynamics

From DFT calculations and electrical measurements, we conclude that hydroxide and oxide ion interstitials are unlikely to be the dominating charge compensating defects in acceptor doped langasite. The compositions investigated in this contribution are therefore assumed to be dominated by effectively negative acceptors, SrLa or GaSi, which are charge-compensated by oxygen vacancies and protons (Eq. (11)). Hydration proceeds according to Eq. (1), for which the equilibrium constant may be written as:

$$K = \frac{\left(\frac{[\text{OH}^-]}{[\text{H}^+] [\text{O}^i]}\right)^2}{\left(\frac{[\text{V}_0]}{[\text{O}^i]} \left(\frac{p_{\text{H}_2\text{O}}}{P}\right)\right)} = \exp\left(\frac{\Delta_{\text{hydr}}S^o}{R}\right) \exp\left(-\frac{\Delta_{\text{hydr}}H^o}{RT}\right)$$
where the site fractions of \( \text{OHO}^- \) and \( \text{vO}^{••} \) are taken as the concentration of defects relative to the concentration of defect sites. The concentration of defect sites is the concentration of regular positions, \( c_i \), and the number of configurations per regular position, \( N_{c,i} \).

Further, \( \Delta_{\text{HydrS}} \) and \( \Delta_{\text{HydrH}} \) are the standard hydration entropy and enthalpy, respectively. The concentration of regular positions may, in the dilute limit, be taken as the concentration of lattice positions the defect may form on. In Section 4.1, we found that both oxygen vacancies (sites O3Ga and O3Si) and protons (sites b1, b2, e1 and e2) preferentially form on the O3 ions (with a 6g symmetry). Hence, \( c_{\text{H}} \) and \( c_{\text{v}} \) may both be taken as 6 mol/mol oxide. Since protons may take on two distinct configurations at each O3 (b1/b2 and e1/e2), \( N_{c,H} \) is taken as 2, while \( N_{c,v} = 1 \). From Eq. (15) and the electroneutrality condition (Eq. (11)), the concentration of protons is, for low defect concentrations, given as:

\[
[\text{OH}_2^-] = \frac{1}{4} K \left( \frac{p_{\text{H}_2\text{O}}}{p} \right) \left( \frac{c_{\text{H}} N_{c,H}^2}{c_{\text{v}} N_{c,v}} \right)^{-1} \left[ 1 + \frac{8 A}{K \left( \frac{p_{\text{H}_2\text{O}}}{p} \right) \left( \frac{c_{\text{H}} N_{c,H}}{c_{\text{v}} N_{c,v}} \right)} \right]
\]

Curve fitting of Eq. (16) to the TG data (Fig. 9) with the effective acceptor concentration taken as the saturation level of the TG measurements (2 and 5 mol% for 6Ga and 12Ga:LGS), yields values for \( \Delta_{\text{HydrS}} \) and \( \Delta_{\text{HydrH}} \) (see Table 3). The resulting concentrations are included as solid lines in Fig. 9. The extracted enthalpies are moderately exothermic comparable to those found for other proton conducting oxides (0 to \(-250 \text{ kJ/mol}) [25], and are in good agreement with that found by DFT calculations in Section 4.1 (\(-106 \text{ kJ/mol})

5.2. Transport properties of langasite

The bulk conductivity of langasite can, under oxidizing conditions, be expressed by the partial conductivities of protons, oxygen vacancies (ions) and electron holes:

\[
\sigma_{\text{tot}} = \sigma_\text{H} + \sigma_\text{v} + \sigma_\text{p}
\]

or

\[
\sigma_{\text{tot}} = \frac{F \delta_m}{T} \left( [\text{OH}_2^-] \mu_\text{H}^- \exp \left( -\frac{\Delta_{\text{HydrH}}}{RT} \right) + 2 [\text{vO}^{••}] \mu_\text{O}^{••} \exp \left( -\frac{\Delta_{\text{HydrV}}}{RT} \right) + p_{\text{H}_2\text{O}} \mu_\text{p} \exp \left( -\frac{\Delta_{\text{H}_2\text{O}}}{RT} \right) \right)
\]

where \( F \) is the Faraday constant and \( \delta_m \) is the molar density of the material. \( \mu_i \) and \( \Delta H_{\text{m},i} \) are the pre-exponential mobility and the mobility

![Fig. 7. Bulk conductivity as a function of inverse temperature in wet O2 (solid lines) and wet Ar (dotted lines) for 6Ga:LGS and 12Ga:LGS. The \( p_{\text{H}_2\text{O}} \) is kept at 0.03 atm throughout the interval, while the \( p_{\text{O}_2} \) is \( \approx 1 \) and \( \approx 10^{-5} \) atm in O2 and Ar, respectively. The measurements are performed using a constant cooling rate of 12 °C/h and at an AC frequency of 10 kHz.](image)

![Fig. 8. Bulk conductivity of nominally undoped single crystal (SC) and Ga doped polycrystalline (6Ga and 12Ga) langasite as a function water vapor partial pressure \( p_{\text{H}_2\text{O}} \) in pure oxygen \( (\delta_{\text{H}_2\text{O}} \approx 1 \text{ atm}) \) in the temperature interval 500–1000 °C. The water vapor dependency becomes more pronounced at lower temperatures, and at higher \( p_{\text{H}_2\text{O}} \).](image)
enthalpy of species \( i \), respectively. As electron species are in minority, both concentration and conductivity-wise, their mobility enthalpy and pre-exponential mobility cannot be separated from the equilibrium constant for oxidation and are therefore not reported. The effective acceptor concentrations for 6Sr, 6Ga and 12Ga:LGS were taken as those determined from the TG measurements; 1, 2 and 5 mol%, respectively. We assume that the high temperature conductivity of the single crystal and Ga doped polycrystals is proportional to the acceptor concentration, yielding an estimated acceptor concentration of 0.5 mol% for the single crystal.

Table 4 shows the extracted transport parameters for the compositions included in this work, and those reported by Seh and Tuller [12,13]. The mobility parameters for oxygen vacancies/ions were initially extracted from measurements in wet O\(_2\) and Ar. The mobility enthalpies are also similar to the activation energy of the conductivity of Z- and Y-cut single crystals measured in air (with 35% relative humidity) by Schulz (\( E_a = 72 \) kJ/mol) [16]. Finally, while \( \mu_{H^+} \) is in the range typically found for proton conduction in ceramic oxides, \( \mu_{H^+} \) is a factor of 10 higher than that reported by Seh and Tuller [12] for undoped langasite by assuming that [Na\(_{La}\)] = 1.5 \times 10^{19} cm\(^{-3}\), which could indicate trapping of oxygen vacancies by e.g. Ga\(_{Si}\).

The mobility enthalpy of protons is, however, slightly higher for the single crystal, indicative of anisotropic effects. These results are therefore in agreement with the reports by Fritz et al. [14,15] of higher conductivity in wet H\(_2\)(g) for Z- than Y-cut single crystals. The proton mobility enthalpies are also similar to the activation energy of the conductivity of Z- and Y-cut single crystals measured in air (with 35% relative humidity) by Schulz (\( E_a = 72 \) kJ/mol) [16]. Finally, while \( \mu_{H^+} \) is in the range typically found for proton conduction in ceramic oxides, \( \mu_{H^+} \) is a factor of 10 higher than that reported by Seh and Tuller [12] for undoped langasite by assuming that [Na\(_{La}\)] = 1.5 \times 10^{19} cm\(^{-3}\), which could indicate trapping of oxygen vacancies by e.g. Ga\(_{Si}\).

Fig. 10 compares the bulk conductivities and extracted partial proton conductivities in wet O\(_2\) for all compositions investigated in this contribution. Protons dominate the bulk conductivity of all compositions below approximately 800 °C, and the partial proton conductivity increases with increasing dopant concentration. For a given doping level the polycrystalline conductivities and those of single crystals measured in the different crystallographic directions are related through [26]

\[
\sigma(x,y,z) = \sigma_{pc} \left( \frac{x^2 + y^2 + z^2}{3} \right) \left( \frac{T}{\mu_0 H} \right)^{2/3}
\]

Hence, the proton conductivity of a Z-cut single crystal would be slightly higher than that of the polycrystalline samples in Fig. 10.
The partial proton conductivity of langasite would still be modest compared to state-of-the-art perovskite structured proton conductors (10⁻³ to 10⁻² S/cm at 700 °C [27,28]), mainly due to the high activation energy of the proton mobility. In future studies we therefore intend to investigate the effect of substitution of Si by other tetra- and pentavalent cations such as Ti, Sn, and Ta on the transport properties of protons.

Fritze et al. [14] concluded that the impact of proton conductivity on the resonance frequency of a langasite resonator was negligible. However, as protons dominate both the transport and defect chemical properties of acceptor doped langasite, operation of crystals with small off-sets in the Ga/Si ratio as for instance microbalances, would be prone to bulk absorption of H₂O. Shifts in the resonance frequency of a langasite based resonator upon exposure to H₂O(g) would thus be related not only to the increased mass of the resonator stemming from adsorbed surface species, but also to the increased mass of the resonator itself due to hydration according to Eq. (1). Nevertheless, the possible effect of bulk absorption of protons on the sensing properties of langasite based devices can be completely suppressed by effective donor doping through for instance lowering the Ga/Si ratio.

6. Conclusions

This contribution establishes the defect structure, transport and thermodynamic properties of acceptor doped langasite in H₂O(g) containing atmospheres by combining DFT calculations with electrical and thermogravimetric investigations. Nominally undoped single crystalline and Sr and Ga doped polycrystalline langasite were shown to be effectively acceptor doped, with oxygen vacancies being the dominating charge compensating defect at high temperatures and in dry atmospheres, and protons at lower temperatures in wet atmospheres. Protons also dominate the conductivity up to ~800 °C in wet atmospheres, and protons at lower temperatures in wet atmospheres. Effective acceptor doped, with oxygen vacancies being the dominating charge compensating defect at high temperatures and in dry atmospheres, and protons at lower temperatures in wet atmospheres. The hydration enthalpy and entropy are, from curve fitting of water uptake profiles (of Ga doped polycrystalline langasite), ~100 ± 2 kJ/mol and ~157 ± 5 J/mol K, respectively. The partial proton conductivity of langasite itself is modest, but the langasite family of oxides presents an interesting class of novel proton conductors with a broad compositional variety. Nevertheless, protons affect both the electrical properties of langasite, and the weight of the crystal itself, which would have implications for the operation of off-stoichiometric langasite based resonators in moist atmospheres. The effects of water can, however, be completely depressed through effective donor doping by for instance higher Si to Ga ratio than the stoichiometric 1:1 ratio.

References