The Band Gap of BaPrO₃ Studied by Optical and Electrical Methods

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We report on measurements of the electrical and optical properties of BaPrO₃. The temperature dependences of the electrical conductivity σ and the Seebeck coefficient α of polycrystalline samples were studied over a wide temperature range (300 - 1050°C). At lower temperatures, the observed charge transport can be described as thermally activated hopping of small polarons with an activation energy of 0.37 eV. An observed change in temperature dependence of both σ and α around 700°C was observed and interpreted as a transition from extrinsic to intrinsic carrier transport. The intrinsic conduction can be modeled with an apparent electrical band gap of ~ 2 eV. Optical absorption and emission spectroscopy in the UV-VIS-NIR range revealed a series of characteristic absorption thresholds and the type of optical transitions was identified by combining transmittance and diffuse-reflectance spectroscopy methods. An absorption edge of indirect type with onset at

0.6 eV is attributed to small polaron effects. The higher-lying absorption thresholds of direct origin positioned at around 1.8 and 3.8 eV are correlated with thermal activation parameters from electrical measurements and discussed in terms of the band gap of BaPrO₃.

Keywords: Optical band gap, electrical band gap, small polaron

Introduction

Ba-based compounds with the perovskite-related generic formula BaBO₃ show a large variety of functional properties, depending on the chosen *B*-site cation. For example, they are used as ionic conductors (*B* = Zr⁴⁺ and Ce⁴⁺), lead-free piezoelectrics (*B* = Ti⁴⁺), or show interesting magnetic ordering phenomena (*B* = Fe³⁺ or Mn³⁺). In the present contribution, we study BaPrO₃, which has attracted interest as a model system for tetravalent lanthanides with charge state Pr⁴⁺ ([Xe]4f¹). This is fruitful, for example, in the study of *f*-electron magnetism and crystal field effects.⁶⁻⁸ Its high temperature conduction properties have been studied in the area of solid oxide fuel cells, as allegedly high proton conductivities for (Y,Yb,Gd)-doped BaPrO₃ were reported.⁹ Later investigations concluded that these compositions dominantly had *p*-type semiconductor characteristics, instead of protonic conduction.¹⁰⁻¹⁴ Consequently, BaPrO₃-based compositions have been proposed as one of the cathode components in proton conducting solid oxide fuel cells.¹⁵⁻¹⁹

The present work was initially motivated by the complex behavior of the conductivity at high temperatures observed in BaPr_{0.9}Gd_{0.1}O_{3-δ}.¹² Most of the features were correlated with the temperature-induced phase transitions, studied for BaPr_{0.9}Y_{0.1}O_{3-δ} and BaPrO₃.²⁰ It was reported that for BaPrO₃ the crystal symmetry changes from orthorhombic to cubic via the phase transitions $Pbnm \rightarrow Imma \rightarrow R\bar{3}c \rightarrow Pm\bar{3}m$ which occur at 240, 375, and 860°C,

respectively.^{20, 21} However, a gradual increase of conductivity for BaPrO₃ above 700°C was found, which could not be associated with a structural phase transition. It was therefore speculated that a transition from an extrinsic to intrinsic electronic conductivity occurred around this temperature. In order to confirm this assumption, knowledge of the electronic band structure of BaPrO₃ and the nature of the charge carriers is required. A recent computational study using density functional theory (DFT) predicts that BaPrO₃ is a wide band gap semiconductor ($E_g = 3.2$ eV),²² however, no experimental evaluation has been reported yet. Therefore, it is clear that more comprehensive studies with a focus on the fundamental electronic structure of BaPrO₃ are needed.

Herein, we present a holistic study of nominally undoped BaPrO₃, including measurements of the electrical conductivity, the Seebeck coefficient, and optical spectroscopy, to investigate the nature of charge transport in BaPrO₃ and to re-assess the speculations from Ref. ²⁰.

Experimental

Sample Preparation

Polycrystalline samples of BaPrO₃ were synthesized using a wet chemical combustion route, as reported elsewhere.²⁰ The powders were cold pressed into cylindrical pellets and sintered at 1400°C for 5 h with a heating and cooling rate of 5 K/min. The samples were dry polished using SiC paper prior to the measurements to remove possible material with off-nominal composition on the surface. Relative density of all studied samples was above 93%, making the influence of porosity on the electronic properties minor. Phase purity was checked by X-ray diffraction (XRD) using a Siemens D5000 with Cu K_{α1} radiation, showing single-phase perovskite after sintering (see Fig. 1). The X-ray patterns were indexed based on the *Pbnm*

space group and the lattice parameters calculated using Le Bail refinement; $a = 6.175 \text{ \AA}$, $b = 6.212 \text{ \AA}$, $c = 8.726 \text{ \AA}$, similar to lattice constants reported by Jacobson *et al.*²³

Electrical and thermoelectric characterization

To measure the electrical conductivity σ and the Seebeck coefficient at high temperatures and controlled atmospheres, we used a custom built assembly mounted into a NorECs ProboStatTM measurement cell, described elsewhere in detail²⁴ and summarized in the following. The disk-shaped samples were placed onto an alumina plate, with four platinum electrodes pressed onto the rim of the top surface for conductivity measurements by the van der Pauw method. Two S-type thermocouples were attached to both surfaces of the sample. A resistive micro-heater made of thin Pt10Rh wire was placed below the sample to allow a variation of the temperature difference across the sample. This geometry allows subsequent measurement of cross-plane Seebeck coefficient and in-plane conductivity under identical experimental conditions. A stationary state was ensured by monitoring the conductivity measured by the voltage across two of the electrodes, with a constant current applied across the other two. The electrical properties are fully reproducible during heating and cooling, so that an influence of thermal history on the derived results can be excluded.

Optical characterization techniques

The initial assessment of the optical properties of BaPrO₃, including determination of the absolute values of absorption coefficient, was obtained from the room-temperature transmittance measurements involving a super-continuum laser source (Koheras SuperK, wavelength range 0.5-1.7 μm) in combination with a fiberoptic spectrometer (Ocean Optics, USB4000). The spectral range was extended towards the near-infrared (NIR) by employing an Acton SpectraPro-275 spectrometer equipped with a Ge-detector, so that transmittance

experiments were eventually covering the NIR-Vis spectral region from 0.7 to 2.5 eV. To meet the requirements of the transmittance measurements, several as-prepared specimens were dry-ground and polished to form a set of optically-thin stand-alone films of variable thicknesses in the range from 50 to 200 μm . The absorption properties of BaPrO_3 in the UV-Vis region ranging from 1.4 to 6.5 eV were examined by room-temperature diffuse-reflectance measurements using a Thermo Scientific EVO-600 spectrophotometer. The optical emission properties were assessed from the photoluminescence (PL) measurements carried out at room temperature by employing the 325 nm line of a cw He-Cd laser (10 mW) as an excitation source. The luminescence was collected by a microscope objective and analyzed with a fiberoptic spectrometer (Ocean Optics, USB4000).

Results and discussion

Electrical conductivity and Seebeck coefficient

Figure 2 shows the electrical conductivity of BaPrO_3 for three samples as a function of temperature. The results obtained for the different samples are consistent. σ increases with increasing temperature and there is a significant, gradual increase in slope at around 700°C. At the highest temperature, the conductivities converge and become nearly identical for all samples.

This behavior roughly divides the temperature range into two. The main characteristic of the conductivity is similar to that of a semiconductor with extrinsic (Ext) conduction in the lowest temperature range and intrinsic (Int) conduction in the highest temperature range. For simplicity we will refer to these temperature regions as the extrinsic and the intrinsic region, respectively, while debating the nature of the conduction. The Seebeck coefficient of sample B is also shown in Fig. 2. Its value is always negative, indicating negative charge

carriers and is constant around $-320 \mu\text{V/K}$ at lower temperatures. For $T > 600^\circ\text{C}$, the absolute value of the Seebeck coefficient decreases substantially. In analogy with textbook semiconductor behavior, these characteristics of the Seebeck coefficient can thus also be described as extrinsic and intrinsic in the respective temperature ranges.

We note, however, that a constant Seebeck coefficient alone is not sufficient to conclude a constant carrier concentration. Nagaraja et al. have suggested for Rh_2ZnO_4 that a change in carrier concentration is compensated by a variation of the effective density of states, resulting in an effectively constant Seebeck coefficient.²⁵

The decrease of the absolute value of the Seebeck coefficient at high temperatures (from $320 \mu\text{V/K}$ in the extrinsic region to $150 \mu\text{V/K}$ at 1000°C) can indicate an increase in the carrier concentration, which is consistent with the stronger increase in conductivity with temperature in the intrinsic temperature region. Our results for the Seebeck coefficient are in qualitative agreement with data reported for SrPrO_3 , which we expect to be similar to BaPrO_3 : For that material, a negative Seebeck coefficient of about $-215 \mu\text{V/K}$ was reported, fairly temperature independent between 460 and 590°C .²⁶

Quantitative analysis of the electrical transport data and hypothetical scenarios

In the following, we will construct a simple framework that is relatively generic and that can be used to extract quantitative parameters from the electrical measurements. The conductivity σ as a function of temperature T can generally be written as

$$\sigma(T) = q \cdot \sum_j \mu_j(T) \cdot n_j(T) \quad (1)$$

where q is the elementary charge, $n_j(T)$ is the charge concentration in band j , and $\mu_j(T)$ is the associated mobility. The bands can be various valence, conduction and impurity bands and the charge carriers can be electron or hole based. We will only consider situations where we have a temperature independent extrinsic concentration of negative charge carriers, n_{Ext} , consistent with our observations. These electrons can originate from impurities or frozen-in structural defects acting as donors and will dominate the transport at low temperatures. In addition we have temperature dependent concentrations of electrons and holes, which we call intrinsic. For our samples in the extrinsic region (from 300 to 600°C), the electron concentration is assumed constant, and provided by donor species that are ionized at the lowest temperatures in this study. The value of n_{Ext} is different for the individual samples, reflecting different impurity concentrations. At higher temperatures, we assume that the electron concentration increases with $n_{\text{Int}}(T)$ due to thermal activation, yielding a total electron concentration of $n(T) = n_{\text{Ext}} + n_{\text{Int}}(T)$. The hole concentration under these conditions is then $p(T) = n_{\text{Int}}(T)$. At the highest temperatures studied here, the measured conductivities of all three samples are practically identical, indicating an intrinsic behavior of BaPrO₃. Eq. 1 can thus be rewritten as:

$$\sigma = q \cdot \mu_n(T) \cdot n_{\text{Ext}} + q \cdot \mu_n(T) \cdot n_{\text{Int}}(T) + q \cdot \mu_p(T) \cdot p_{\text{Int}}(T) \equiv \sigma_{\text{Ext}}(T) + \sigma_{\text{Int}}(T) \quad (2)$$

where μ_n and μ_p are the mobilities of electrons and holes, respectively. We have thus divided the conductivity in two parts where σ_{Ext} dominates at the lowest temperature in our measurements and σ_{Int} dominates at the highest temperature.

The Arrhenius type temperature dependence of the conductivity in the extrinsic region, while the Seebeck coefficient is nearly temperature independent, indicates an activated mobility. The latter is often assumed to reflect polaronic conductance.²⁵ In analogy to

findings for acceptor-doped BaPrO₃, we assume charge transport in the nominally undoped BaPrO₃ to occur via activated hopping of self-trapped charge carriers.^{12, 20} The concept of self-trapping describes an electron (or hole) being trapped within a self-created crystal polarization, where such an electron with locally distorted lattice around comprises a quasiparticle known as a small polaron. In contrast, when the coupling between lattice and carrier only leads to a renormalization of the effective mass of the carrier and not to a complete localization, one refers to the entity of carrier and lattice polarization as a large polaron. For small polarons, the carrier mobility μ can be expressed as^{25, 27}

$$\mu = \frac{M_0}{T} \cdot \exp\left(\frac{-E_a}{k_B T}\right); \quad M_0 = \frac{g \cdot (1 - c) \cdot q \cdot a^2 \cdot \omega_{LO}}{k_B} \quad (3)$$

where E_a is the activation energy for hopping of electrons being half of the polaron binding energy. M_0 is a constant for a given sample, being dependent on the lattice vibration frequency ω_{LO} , a is the lattice constant, g is a geometric factor, and $(1-c)$ is the probability that the neighbor site is available for the polaron (for small concentrations as here, $1-c \approx 1$). At low temperatures, we have

$$\sigma \approx \sigma_{Ext} = \frac{n_{Ext} \cdot M_0}{T} \cdot \exp\left(-\frac{E_a}{k_B T}\right) \quad (4)$$

The hopping activation energy E_a for this temperature region is from our measurements determined to be 0.37 eV, which is similar to earlier findings by Knee *et al.* (0.34 eV) for BaPrO₃ with 10% Gd or Y doping, i.e. BaPr_{0.9}Gd_{0.1}O_{3-δ} and BaPr_{0.9}Y_{0.1}O_{3-δ}.²⁰ Also the measurements in air on samples with various doping levels of Gd by Fukui *et al.*⁹ are in agreement with this. The present measurements and these reports together indicate that in

BaPrO₃, the mobility of electron based small polarons and hole based small polarons have a similar temperature dependence, i.e. $\mu_n(T) \approx a \cdot \mu_p(T)$, with a being constant. This allows further simplification of the intrinsic conductivity σ_{Int} in Eq. 2.

$$\sigma_{\text{Int}}(T) = \sigma_{n,\text{Int}}(T) + \sigma_p(T) = q \cdot \mu(T) \cdot (1 + a) \cdot n_{\text{Int}}(T) \quad (5)$$

By relating the conductivity results in this work to previous reports,^{12, 20} the concentration of extrinsic defects in BaPrO₃ is estimated to be in the order of 10^{20} cm^{-3} ($\sim 1 \text{ mol-\%}$). The mobilities in the low temperature region have accordingly been calculated to be in the range from 10^{-3} to $10^{-4} \text{ cm}^2/\text{Vs}$, which is indeed a typical low value for a small polaron conduction mechanism. We suggest that these extrinsic defects may involve Pr_{Ba} , formed due to barium evaporation during synthesis. The incorporation of Pr on Ba sites may give defects that act as shallow donors yielding the observed n -type conduction.

From Eqs. 2 and 4 we found σ_{Int} by subtracting the extrapolated extrinsic conductivity from the experimental data of Fig. 2. The curve for $\sigma_{\text{Int}}(T)$ turned out practically identical for all investigated samples and shows a thermally activated behavior. As an example, we show the experimental results of sample B together with the deconvoluted separate contributions from extrinsic and intrinsic conductivity in BaPrO₃ in Fig. 3.

In the following, we will present and discuss three plausible scenarios for the appearance of the intrinsic behavior: i) Formation of ionized oxygen vacancies, which are charge compensated by an increase of the electron carrier concentration ii) Activation of electrons and holes over the fundamental band gap in BaPrO₃. iii) Electron activation into defect-/impurity-band states within the band gap of BaPrO₃.

Scenario i) is the formation of oxygen vacancies at high temperatures, charge compensated by an increase of electronic charge carriers. In the Kröger-Vink notation,²⁸ this process can be written as

with the corresponding mass action law

$$K = \frac{[\text{v}_\text{O}^{\bullet\bullet}] \cdot [\text{e}']^2 \cdot \sqrt{p\text{O}_2}}{[\text{O}_\text{O}^x]} \propto \exp\left(-\frac{\Delta H}{k_\text{B}T}\right) \quad (7)$$

Here, K is the equilibrium constant of reaction in Eq. 6, ΔH the enthalpy change associated with the reaction, $p\text{O}_2$ the oxygen partial pressure, and $[\text{e}']$ corresponds to n_int in Eq. 2. In the high temperature limit, where the extrinsic contribution by unintended impurities can be neglected, the overall charge neutrality requires

$$2[\text{v}_\text{O}^{\bullet\bullet}] = [\text{e}'] \quad (8)$$

Thus, at constant oxygen partial pressure, the electronic charge carrier concentration increases with a Boltzmann factor, providing a possible explanation for the observed increase of σ_int . At constant temperature, however, combining Eqs. 7 and 8 yields $n_\text{int} \propto p\text{O}_2^{-1/6}$. Thus, if the high temperature electronic properties of BaPrO_3 were dominated by electron charge carriers compensating the formation of oxygen vacancies, the conductivity should show a distinct variation with the oxygen partial pressure, approaching $\propto p\text{O}_2^{-1/6}$ at the highest temperatures. However, the observed conductivity does not show any significant

dependency on the oxygen partial pressure (Fig. 3, inset) even at 1050°C, so that this model for the observed high temperature behavior can be ruled out.

Scenario ii) and iii) can be analyzed together, though with a different physical meaning of the extracted parameters. In all cases we assume the charge carriers to have the same temperature dependence of the mobilities and being of the same small polaron form as in the extrinsic temperature regime.

In scenario ii) electron carriers are created by thermal excitation from the valence band and $n_{\text{Int}}(T) = p_{\text{Int}}(T)$ in Eq. 2. For illustrative purposes, one may identify electrons with a Pr^{3+} and holes with an O^- state in this scenario. For a semiconductor, the concentration of intrinsically generated electrons and holes can be written in the following generalized form:

$$n_{\text{Int}} = A \cdot T^x \cdot \exp\left(\frac{-E_g}{2k_B T}\right) \quad (9)$$

where A is a constant dependent on the density of states of the charge carriers and E_g is the electrical band gap. The best value of the exponent x will depend upon the energy distribution of electronic states. For a non-degenerate semiconductor with a single parabolic band, the temperature exponent is $x = 3/2$. If that situation is assumed, a good fit of Eqs. 3, 5, and 9 to the experimental σ_{Int} is obtained using $E_g \sim 1.7$ eV. However, as electrons in BaPrO_3 are assumed to be transported as small polarons via thermally activated hopping between localized states, the associated bands are likely to be narrow. One might approximate that situation by an energy independent density of states or a delta function, in either case it can be described by $x = 0$ in the exponent. Also this model reproduces the observed conductivity well using Eq. 9 and $E_g \sim 2.0$ eV. The available experimental data does not allow to distinguish

between $x = 3/2$ and 0, or the corresponding E_g . We conclude that the apparent electronic band gap of BaPrO₃ is between 1.7 and 2.0 eV.

By assuming scenario iii) we would determine the ionization energy of a defect state in the band gap, while the numerical analysis procedure would be exactly the same as that for scenario ii). Now, the derived carrier activation energy in the range 1.7 – 2.0 eV corresponds to the energy difference between the fundamental valence band and these defect states. The density of these states might be high enough to form a band, usually called an impurity band,^{29, 30} while the self-trapping polaron mechanism can lead to hopping between localized states derived from the impurity band. While holes may still be identified here with an O⁻ state, the nature of this impurity band is less clear. In the *Overall Discussion* later on we suggest that it is related to states localized at barium vacancies, formed by evaporative loss of Ba during synthesis.

The similarity in mobility activation energies of the *n*- and *p*-type carriers in BaPrO₃ is uncommon, but we speculate that the hole state could have a strong Pr⁵⁺ character (Pr has 5 valence electrons), instead of O⁻ as suggested earlier. Hence *n*- and *p*-type transport can be thought of hopping between Pr³⁺/Pr⁴⁺ and Pr⁴⁺/Pr⁵⁺ pairs, respectively, with similar polaronic environments, and thus similar activation energies for the mobility.

Optical transmittance and diffuse-reflectance

The fundamental mechanism of optical absorption in a semiconductor with band gap E_g is a valence-to-conduction band electronic transition, i.e. a photon of energy $h\nu$ directly creates an electron-hole pair. In a parabolic band approximation, this intrinsic absorption coefficient can be described as

$$\alpha = \frac{A}{h\nu} \cdot (h\nu - E_g)^m$$

(10)

Here, A is a material specific constant and the power index m depends on the particular type of optical transitions involved in absorption: $m = 1/2$ for direct allowed, $m = 3/2$ for direct forbidden, $m = 2$ for indirect allowed, and $m = 3$ for indirect forbidden transitions.

For highly-scattering materials like powders or ceramics, it is often not possible to extract reliable absolute values for the absorption coefficient. In these cases, the Kubelka-Munk treatment of the diffuse-reflectance spectra³¹ allows for unambiguous extraction of the band gap energies, albeit lacking to provide absolute values of the absorption coefficient. The Kubelka-Munk- or remission function F is used to convert measured diffuse reflectance of a sample R_s and reference R_r into equivalent absorption distributions by relating these parameters to the absorption α and scattering S coefficients as

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{\alpha}{S} \quad (11)$$

where $R = R_s/R_r$. The spectral shape of the remission function $F(R)$ near the absorption edge is given by a general expression similar to that for absorption in Eq. 9:

$$F = \frac{C}{h\nu} \cdot (h\nu - E_g)^m \quad (12)$$

where C is a constant and the exponent m depends on the type of optical transitions as mentioned earlier. The particular type of transitions and, consequently, the electronic band gap structure can be inferred from the linear behavior of $(F h\nu)^m$ once plotted as a function of photon energy $h\nu$, whereas the band gap energy E_g can be deduced by extrapolating $(F h\nu)^m$ to zero. This approach, also known as Tauc plot,³² is equally applicable for the analysis

of transmittance results. In the present work, both transmittance and diffuse-reflectance techniques were employed to ensure comprehensive and complementary insight into absorption properties.

Figure 4 summarizes optical absorption properties of BaPrO₃ in the Vis-NIR spectral region derived from the room-temperature transmittance measurements. A set of optically-thin ($\alpha d \leq 1$) specimen of variable thickness was measured (Fig. 4a) to extend the range and ensure the reliability of the extraction of the absolute values of absorption coefficient at different wavelengths (Fig. 4b). The presented absorption edge is comprised of several superimposed spectra corrected for different thicknesses, and scattering losses of the samples and then calibrated to the absorption value of the 997 nm-laser line. The auxiliary data set obtained using the Acton SpectraPro-275 spectrometer extending further into the near-infrared region (grey curve in Fig. 4b) completes the delineation of this composite absorption edge. Although the data contains more noise, one can clearly observe the onset of absorption at around 0.6 eV with a subsequent build-up throughout the visible range of the spectrum ($\alpha \geq 2 \times 10^3 \text{ cm}^{-1}$) and suggesting involvement of indirect-type optical transitions according to the band-edge simulations using Eq. 10 (dotted curves in Fig. 4, with $E_g = 0.7 \text{ eV}$).

Due to increasing scattering losses in ceramic specimens at shorter wavelengths, we switched to the diffuse-reflectance spectroscopy (DRS) method to follow further the developments of absorption in the Vis-UV region of the spectra. Figure 5 summarizes the results of diffuse-reflectance measurements of BaPrO₃ carried out at room temperature. Note good agreement of the key spectral features of the absorption edge with those in Fig. 4 from transmission measurements. Besides verification and confirmation of the latter, the diffuse-reflectance measurements also reveal new details in the higher energy side of absorption spectra now extending up to 6.5 eV. The absorption edge of BaPrO₃ appears to be of indirect nature with a clear onset at $\sim 0.7 \text{ eV}$ followed by several higher-lying absorption

thresholds of direct origin positioned at around 1.8, 2.3 and 3.8 eV as can be seen in the Tauc plot in Fig. 5b.

The optical absorption at photon energies below that of the band gap is usually associated with transitions between localized states, which may form due to a disordered structure of the material; also strong electron–phonon interaction can lead to localization in the form of small polarons. It is known that electron polarons in oxide perovskites demonstrate optical absorption in the near-infra-red region, typically around 0.5 - 0.9 eV, whereas hole polaron absorption lies at even higher energies.³³ In the framework of the theory of self-trapped electrons with a binding energy E_a , the optical absorption spectrum starts at $2E_a$ and extends upwards having a maximum at approximately $4E_a$.^{34, 35} Assuming the polaron activation energy from the temperature dependent conductivity measurements as $E_a \sim 0.37$ eV (Section 3.2), the polaron absorption threshold is expected to occur at $2E_a \sim 0.7$ eV with a maximum absorption at $4E_a \sim 1.5$ eV. This indeed agrees well with the experimental observations presented in Figs. 4 and 5.

Photoluminescence

The photoluminescence (PL) from BaPrO₃ was examined at room temperature, revealing very low quantum efficiency, which implies high non-radiative losses and/or very fast carrier trapping on localized mid-gap defects. A typical PL spectrum is presented in Fig. 5a, demonstrating a broad, almost featureless emission band centered at 2.3 eV with a full width at half-maximum (FWHM) of about 0.6 eV. Among the mechanisms proposed to explain the origins of luminescence in perovskites, the recombination of self-trapped electrons or holes (i.e. small polarons) seems to be most supported in the literature.^{36, 37} Supposing this model holds for BaPrO₃, the strength of the electron–phonon interaction can be ascribed to the Stokes shift, i.e. the difference between the absorption and emission maxima. The Stokes

shift turns out to be large (~ 1.5 eV or 1.2×10^4 cm⁻¹), considering the PL emission peak at ~ 2.3 eV and the highest absorption threshold at ~ 3.8 eV. It is noteworthy that similarly large Stokes shifts of the order of 10^4 cm⁻¹ apparently is a common feature for many ABO₃ perovskites.^{38, 39}

Overall discussion

In the following section we compare and discuss the thermal activation and optical transition energies revealed by electrical and optical methods. The presented measurement results point to a central role of small polarons to explain the electrical and optical properties of BaPrO₃. Indeed, the indirect-type threshold at 0.7 eV ($= 2E_a$) is a characteristic feature of small polaron optical absorption. Furthermore, the large Stokes shift ($\sim 10^4$ cm⁻¹) between maximum absorption and emission is a signature of strong electron-phonon coupling in the material, providing yet further support for the formation of small polarons in BaPrO₃.

In line with these findings, also the temperature dependent electrical conductivity and the Seebeck coefficient can be explained assuming conduction in BaPrO₃ being dominated by small polarons. The determined activation energy for electron hopping is $E_a = 0.37$ eV. At high temperatures ($T > 600^\circ\text{C}$), charge carriers are excited across an energy gap of 1.7 - 2.0 eV, which may be associated with the direct-type absorption threshold at 1.8 and 2.3 eV seen in the optical measurements (Fig. 5b). These values appear to be a reasonable approximation for the band gap, considering the observed band gaps of different Ba-based perovskites and the expected reducibility of various B-site cations: While BaZrO₃ is an insulator with $E_g > 5$ eV,⁴⁰ the band gap reported for BaCeO₃ is 4.1 eV,⁴¹ decreasing further to 3.3 - 3.4 eV for BaTiO₃,^{42, 43} and down to 1.5 eV for BaCoO₃,⁴⁴ thus following the expected trend of the B-site reducibility (with an oxidation state of IV) according to Co > **Pr** > Ti > Ce > Zr. The optically more intense direct transition with an onset at 3.8 eV may thus correspond to an excitation

of an electron to higher lying bands. Even at the highest temperatures studied here (1050°C), these states are not thermally populated and therefore do not contribute to the electronic transport. We further note that the electrical band gap of ~ 2 eV in the present work is consistent with the ~ 2.2 eV band gap energy estimated from the soft X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) measurements by Miyoshi *et al.*⁴⁵

On the other hand, considering the direct nature and prominence of the absorption onset at 3.8 eV as compared to the onsets at lower energy, it is *per se* reasonable to associate the fundamental band gap of BaPrO₃ to this particular transition. Scenario iii) listed in section 2.2 appears to be compatible with this association. In scenario iii), the high temperature transport is dominated by the thermal excitation (with activation energy ~ 2 eV) of carriers of the valence band to high density defect states (or an impurity band) within the 3.8 eV band gap. Similar as for the origin of the extrinsic charge carriers, we can also only speculate on the nature of the defects forming this impurity band. A plausible hypothesis is that these states are related to barium evaporation during synthesis.

For example, the observed *n*-type conduction could occur via mid-gap states localized at barium vacancies ($v_{\text{Ba}}^{\prime}$ or $v_{\text{Ba}}^{\prime\prime}$ in Kröger-Vink notation, depending on the ionization level). This impurity band may be located around 2 eV above the valence band, bearing in mind the similarity with the 1.7 - 2.0 eV electrical band gap from the conductivity measurements and assuming thermal excitation of the valence band electrons in this process. Thus, for scenario iii), the fundamental band gap of BaPrO₃ is ~ 3.8 eV, while the electrical transport is in fact governed by point defects, introduced into the material during synthesis. A similar discrepancy between the optical (4.1 eV) and electrical (2.3 eV) band gap was reported for Y-doped BaCeO₃ by He *et al.*^{41, 46} These authors explained their data by Urbach tail states,

associated with the presence of disordered oxygen vacancies in the material, extending into the fundamental band gap.

Unfortunately, the available experimental data do not allow for an unambiguous discrimination between the two different assignments of the fundamental band gap in BaPrO₃ outlined above. We may argue that the impurity band scenario iii) appears less likely. One of the arguments against it is that all the samples prepared here (sintered at 1400°C for 5 h) show almost identical values for the intrinsic conductivity as the sample reported by Knee *et al.*,²⁰ sintered at 1300°C for 5 h (see sample C, Fig. 2). The conductivity should change with the defect concentration, if defect states were important in the conduction or in the thermal activation of carriers. As barium evaporation is expected to increase with increasing temperature and sintering time, the density of defect induced states within the band gap should vary significantly for samples prepared differently. One indication thereof is that the conductivities in the extrinsic region actually are different, likely caused by differences during sample preparation. Since no significant difference in the intrinsic conductivity is observed for all samples, it appears unlikely that impurity states are dominating the intrinsic conduction or activation.

Thus, most experimental observations indicate that the fundamental band gap of BaPrO₃ is indeed around 2 eV (scenario ii)), as seen in the electrical and (to a less degree) optical measurements.

Summary and conclusions

In summary, we have investigated the band gap of BaPrO₃ by measurement of both the electrical transport at temperatures from 300 to 1050°C and the absorption and emission properties at room temperature. The material exhibits predominantly n-type electronic

conductivity over the entire measured temperature range. The concurrent changes in the temperature dependencies of the Seebeck coefficient and conductivity above 700°C are attributed to a gradual change from extrinsic to intrinsic transport properties. Assuming the inter-band thermal activation of carriers in the case of intrinsic conductivity, the electrical band gap is estimated to be about 2 eV. Further insight into electronic band structure of BaPrO₃ was obtained by combining photoluminescence, transmittance and diffuse-reflectance spectrophotometry in the NIR-Vis-UV spectral range. The absorption edge of indirect type with onset at 0.7 eV is associated with small polaron effects. The higher-lying absorption thresholds of direct origin positioned at around 1.8 and 2.3 eV are identified with the optical band gap, in good agreement with the value extracted from the electrical transport measurements. The room-temperature PL emission comprises a single broad band centered at ~2.3 eV, related to the recombination of excited charge carriers. An intense absorption threshold at 3.8 eV is associated with the excitation of electrons into higher bands, not contributing to the observed electronic transport.

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Figure 1. XRD pattern of a BaPrO₃ pellet after sintering at 1400°C. The indices of the most intense reflections are given. All peaks could be indexed according to the *Pbnm* space group and no other phase was detected. The indices of the most intense reflections are given.

Figure 2. The electrical conductivity and the Seebeck coefficient of BaPrO₃ at $pO_2 = 1$ atm as a function of inverse temperature. The conductivity was obtained for two different samples (A,B; open symbols) in this work and is compared to results obtained previously using a different sample (C; dashed line)²⁰. The Seebeck coefficient (closed circles) was measured for sample B.

Figure 3. The measured total conductivity of BaPrO₃ (Sample B) at $p\text{O}_2 = 1$ atm against inverse temperature with calculated extrinsic and intrinsic contributions. **Inset:** The total conductivity at different oxygen partial pressure $p\text{O}_2$.

Figure 4. Optical transmittance and absorption of BaPrO₃ measured at room temperature in the ViS-NIR spectral region: **a)** transmittance spectra of different thickness specimen, **b)** absorption coefficient as a function of photon energy. The composite absorption edge comprises superimposed spectra corrected for variable sample thickness and scattering losses and auxiliary data set extending into the near-infrared (grey curve); dotted lines designate the simulated absorption edge assuming indirect optical transitions.

Figure 5. **a)** Optical absorption and emission spectra of BaPrO₃ obtained by diffuse-reflectance spectroscopy (DRS) and photoluminescence (PL) at 300 K. The apparent absorption thresholds are marked by arrows; dashed-curves are simulated guides for eyes indicating indirect and direct absorption edges. **b)** Tauc plot of the Kubelka-Munk function assuming indirect and direct optical transitions. The absorption thresholds at 0.7, 1.8, 2.3 and 3.8 eV are defined by extrapolating straight-line intercepts to zero-absorption.