Light Absorption and Emission by Defects in Doped Nickel Oxide

Robert Karsthof,* Ymir Kalmann Frodason, Augustinas Galeckas, Philip Michael Weiser, Vitaly Zviagin, and Marius Grundmann

Nickel oxide is a versatile p-type semiconducting oxide with many applications in optoelectronic devices, but high doping concentrations are often required to achieve necessary electrical conductivity. In contrast to many other transparent oxide semiconductors, even moderate doping levels in NiO can lead to significant optical absorption in the visible spectral range, limiting the application range of the material. This correlation has been reported extensively in the literature, but its origin has been unknown until now. This work combines experimental data on optical properties from a variety of NiO samples with results from hybrid density functional theory calculations. It shows that strong electron–phonon interaction leads to a significant blueshift (0.6–1 eV) of electronic transitions from the valence band maximum to defect states by light absorption with respect to the thermodynamic charge transition levels. This essentially renders NiO a narrow-gap semiconductor by defect band formation already at moderate doping levels, with strong light absorption for photon energies of approximately 1 eV. The calculations are also shown to be fully consistent with experimental data on defect-related light emission in NiO.

1. Introduction

Nickel oxide is one of the few examples of a wide-gap semiconducting metal oxide with holes as majority carriers. Combined with its high optical transparency in its pure, defect-free form, and its comparably high-lying valence and conduction bands, it has become widely used in various optoelectronic devices as electron-blocking, hole-conducting top electrode whenever transmitting visible light is critical for device functionality. The most prominent example is perovskite solar cells where NiO has been widely explored as a hole transport layer.\(^1\) To achieve at least moderately conductive NiO films, doping by monovalent ions such as Li, Na, K, Cu, or Ag can be employed.\(^1\)-\(^8\) Alternatively, inducing an excess of oxygen/deficiency of nickel leads to the formation of nickel vacancies V\(_{\text{Ni}}\) that act as acceptors, albeit not producing the same level of conductivity as the first method. In contrast to “conventional” wide-gap semiconductors, such as ZnO or In\(_2\)O\(_3\), where high optical transmittance in the visible spectral range is retained also for carrier concentrations in the degenerate regime, doping-induced optical absorbance in NiO is pronounced, leading to a reduction of average visible transmittance \(T\) of the order of 50% already at hole concentrations around \(10^{18}\) cm\(^{–}\).\(^8,9\) From a device fabrication perspective, this makes it necessary to accept a trade-off between the optical and electrical performance of NiO thin films, as both high \(T\) and \(\sigma\) cannot be achieved at the same time. In a recent study,\(^10\) we have determined the \(\langle 0/-\rangle\) charge transition levels (CTLs) of the Li\(_{\text{Ni}}\) and V\(_{\text{Ni}}\) acceptors as 0.19 and 0.41 eV above the valence band maximum (VBM), respectively, i.e., shallow enough to be at least partially ionizable at room temperature. In this article, we demonstrate that doping NiO with Li or with Ni vacancies leads to the formation of detectable defect bands in the bandgap that enable optical transitions in the near-infrared spectral range (1–2 eV). Based on hybrid functional calculations, we construct configuration coordinate diagrams describing optical charge-state transitions involving the Li\(_{\text{Ni}}\) and V\(_{\text{Ni}}\) acceptors. Despite their relatively small ionization energies, these acceptors are predicted to exhibit polaronic localized hole states, resulting in strong electron–phonon coupling and optical transitions with significant Franck–Condon shifts. This leads to a large blueshift of the electronic transitions induced by photon absorption when compared to the thermodynamic charge transition levels, as they have been observed in ref. \(^{10}\). Additionally, the hybrid functional calculations suggest photon emission by charge carrier defect recombination with emission spectra that agree well with experimental photoluminescence (PL) data.

RESEARCH ARTICLE

R. Karsthof, P. M. Weiser
Centre for Materials Science and Nanotechnology
Universitetet i Oslo
P.O Box 1126, Blindern, Oslo 0318, Norway
E-mail: r.m.karsthof@smn.uio.no
R. Karsthof, V. Zviagin, M. Grundmann
Felix-Bloch-Institut für Festkörperfysik
Universität Leipzig
Linnéstr. 5, Leipzig 04103, Germany
Y. K. Frodason, A. Galeckas
Department of Physics
Universitetet i Oslo
P.O Box 1048, Blindern, Oslo 0316, Norway

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adpr.202200138.

© 2022 The Authors. Advanced Photonics Research published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/adpr.202200138
2. Experimental Section

2.1. Materials

Various NiO specimens were studied. A 5 mm × 5 mm × 1 mm (100)-oriented as-cut (unpolished) NiO single crystal was purchased from MaTeCK GmbH (Germany). This mirror furnace-grown crystal was black in color, fully opaque, and electrically insulating. NiO thin films were deposited by means of pulsed laser deposition (PLD) and reactive DC magnetron sputtering. For the PLD-grown films, (100)-oriented MgO substrates were used. For PLD growth, pellets of either pure NiO (99.998% purity) or Li-doped NiO (admixture of 10 wt% Li2CO3) were fabricated by mixing and ball milling of the powders, pressing at 7 bar into 26 mm-diameter disks in a hydraulic press, and sintering the disks for 24 h at 1350 °C. PLD was carried out in a home-built vacuum chamber with a KrF excimer laser (λ = 248 nm, pulse energy 650 mJ, repetition rate 10 Hz). The substrate temperature during growth was adjusted to 300 °C. Oxygen was used as background gas, and the O2 partial pressure was 0.01 mbar. Films resulting from PLD growth were either insulating when grown from the pure NiO pellet, or conductive and visible light-absorbing/black when Li doping was employed, and will be referred to as pure NiO and Li-doped NiO, respectively, in the further course of this article.

DC magnetron sputtering was performed in a reactive Ar/O2 atmosphere from a metallic Ni target on fused silica substrates (target-substrate distance 40 mm), with pO2 varying between 1.1 × 10-4 and 2.8 × 10-2 mbar (while the Ar partial pressure was kept constant at 1.8 × 10-2 mbar to achieve variable Ni:O ratios). DC sputtering power was set to 30 W. No substrate heating was employed. Before film deposition, the target was presputtered in situ for 10 min in pure Ar (pAr = 3.2 × 10-2 mbar). Because of the resulting intrinsic doping with the VNi acceptor, these films will be referred to as VNi-doped NiO. They are slightly absorbing/semitransparent depending on pO2 used, and of gray color.

2.2. Thin Film Characterization

X-ray diffraction was recorded with a Philips X’pert diffractometer using Cu Kα radiation (λ = 1.5406 Å). Optical transmittance and (direct) reflectance measurements were performed with Perkin Lambda 19 UV/vis/NIR and Shimadzu SolidSpec-3700 DUV spectrophotometers, using tungsten, halogen, and deuterium light sources. The thin film complex UV dielectric function was determined using a variable-angle spectroscopic ellipsometry (J.A. Woollam Co.) in a polarizer–compensator–sample-analyzer configuration. Measurements were carried out under ambient conditions in the spectral range from 0.5 to 8.5 eV. For the visible spectral range, spectroscopic ellipsometry was carried out using a M-2000 ellipsometer (J.A. Woollam Co.). Evaluation and modeling of the spectra were done with the Woollam CompleteEASE software.

The PL measurements were carried out at 10 K using a 325 nm wavelength of cw-HeCd laser (photon energy 3.81 eV) and a 246 nm (5.04 eV) line of a frequency-tripled Ti:sapphire laser for excitation with a power density of 20 W cm-2 in both cases. The PL emission was analyzed by a fiber-optic (Ocean Optics, usb4000) and imaging spectrometer systems (Horiba iHR320 coupled to Andor iXon888 EMCCD) with spectral resolution below 2 nm.

2.3. Computational Methods

All first-principles calculations were based on the generalized Kohn–Sham theory with the projector-augmented wave method,[11,12] as implemented in VASP.[13] The Ni 3d electrons were treated explicitly as valence electrons. In order to obtain the energetically preferred antiferromagnetic spin ordering along the [111] direction in NiO (AFII phase), shown in Figure 1, bulk calculations were performed using a rhombohedral unit cell with eight Ni and eight O atoms (2 1 1 1 1 repetition of the primitive unit cell). For these calculations, the energy cutoff was set to 520 eV, and the Brillouin zone was sampled by a Γ-centered 3 × 3 × 3 grid of k-points.

Liu et al.[14] recently performed an assessment of several different hybrid functionals in describing the challenging antiferromagnetic transition-metal monoxides MnO, FeO, CoO, and NiO, which are considered to be prototypical strongly correlated electron systems. Based on the agreement with available experimental data (fundamental bandgap, magnetic moments, valence band density of states, and ion-clamped macroscopic dielectric constant) in that study, the HSE03 functional is employed here,[15] meaning that the fraction of screened Fock exchange

Figure 1. Left: conventional unit cell of NiO, showing the AFII ferromagnetic ordering, as indicated by the blue and orange (111) lattice planes. Right: 2 × 2 × 2 repetition of the rhombohedral primitive NiO unit cell, used for bulk calculations.
$\alpha$ is set to 0.25, and the range-separation parameter $\mu$ is set to 0.30. The resulting lattice parameter and indirect bandgap value are listed in Table 1, along with experimental data. All defect calculations were done using rhombohedral 128-atom supercells (4 x 4 x 4 repetition of the primitive unit cell), a plane-wave energy cutoff of 520 eV, and a single special k-point at (0.25, 0.25, 0.25). Defect formation energies and thermodynamic charge-state transition levels were calculated by following the well-established formalism described in ref. [16]. For example, the formation energy of Li$_{\text{Ni}}$ in charge state q is given by

$$E^f[\text{Li}_\text{Ni}^q] = E_{\text{tot}}[\text{Li}_\text{Ni}^q] - E_{\text{tot}}[\text{bulk}] + \mu_{\text{Ni}} - \mu_{\text{Li}} + qE_F$$

(1)

where $E_{\text{tot}}[\text{Li}_\text{Ni}^q]$ and $E_{\text{tot}}[\text{bulk}]$ are the total energies of the defect-containing and pristine supercells, $\mu_{\text{Ni}}$ and $\mu_{\text{Li}}$ are the chemical potentials of Ni and Li, and $E_F$ is the Fermi-level position relative to the bulk VBM. Upper bounds on the chemical potential of Ni and O are given by the energy of fcc metal Ni and the O$_2$ molecule, corresponding to Ni- and O-rich limits, respectively. These upper limits impose lower bounds on the corresponding other species, given by the thermodynamic stability condition $\Delta \mu_{\text{Ni}} + \Delta \mu_{\text{O}} = \Delta H_F(\text{NiO})$, where $\Delta H_F(\text{NiO})$ is the formation enthalpy per formula unit of NiO. $\mu_{\text{Li}}$ was referenced to the solubility-limiting phase Li$_2$O in both the Ni- and O-rich limits. For charged defects, the total energies were corrected using the schemes outlined in refs. [17–19], with the static (ion-clamped) dielectric constant of 11.6 (5.13).[20] Supercell-size tests were performed using a semilocal functional, establishing that the difference between the formation energies obtained using 128- and 512-atom supercells is within 0.02 eV. Optical absorption and emission energies were estimated using the 1D configuration coordinate (CC) model, using model parameters obtained from the hybrid functional calculations, as described in refs. [21,22]. For the small hole polaron, the self-trapping energy and optical emission energy were calculated as explained in ref. [23].

### 3. Results and Discussion

#### 3.1. Structural Properties

Figure 2 shows the results of the structural investigation by X-ray diffraction. The NiO single crystal exhibits narrow reflexes related to the (100) lattice planes. The (200) lattice plane spacing amounts to $d_{200} = 2.09 \text{Å}$, corresponding to an out-of-plane lattice constant of 4.18 Å, close to the bulk value ($a_{0,\text{ref}}^{\text{NiO}} = 4.17 \text{Å}$). Also, the epitaxial films (pure and Li-doped) grown by PLD (Figure 2a) are (100) oriented, without secondary film reflexes. The out-of-plane lattice constant of the undoped sample amounts to $a_{0,\text{ref}}^{\text{NiO}} = 4.168 \text{Å}$ which is only marginally lower than the reported bulk value, which could be because of slight lattice compression correlated with the in-plane tensile strain induced by the MgO substrate with slightly larger $a_{0,\text{ref}}^{\text{MgO}} = 4.21 \text{Å}$. In the Li-doped sample, the out-of-plane lattice constant is $a_{0}^{\text{NiO}} = 4.132 \text{Å}$ which, based on the reference value for Ni$_{0.7}$Li$_{0.3}$O, and using Vegard’s law, gives a Li content x = 0.21. Interestingly, Li incorporation has not led to a significant broadening of the (100) reflex in this work: the FWHM amounts to 0.14° and 0.15° for the undoped and Li-doped sample, respectively. This is in contrast to the results of, e.g., ref. [7] where significant broadening of the (100) reflex was visible already at Li contents of 9 at%. Dutta et al. [27] however, have reported data where up to a Li content of 7 at% no significant broadening of the (111) reflex is visible. We currently have no explanation for these two distinct kinds of behavior.

In Figure 2b, diffractograms of a reactively sputtered NiO film are shown, exhibiting mainly the broad signal at 22° originating from the amorphous glass substrate. The presence of the NiO

---

**Table 1.** Lattice parameters and indirect bandgap $E_g$. Experimental values are listed for comparison. See ref. [14] for comparison of other bulk parameters of NiO.

| $\alpha$ [Å] | Reference | $E_g$ [eV] | References |
|--------------|-----------|------------|------------|
| HSE03        | 4.168     | 4.28       |            |
| Experiment   | 4.171     | 4.0        | [24] [25]  |
|              |           | 4.3        | [26]       |

---

**Figure 2.** X-ray diffraction patterns of different NiO samples. a) Single crystal, as well as undoped and Li-doped doped NiO films grown by PLD on MgO substrates. (**) MgO-related reflexes. (+) secondary reflexes due to Cu Kα and W Kα spectral lines, and (o) reflexes from the sample holder. Inset shows enlarged version of the angular region around the (200) reflexes. b) DC magnetron-sputtered films on fused silica.
(111) and (200) reflexes can be conjectured where they would be expected (highlighted in gray). The fact that the signal is barely above the noise level can be attributed to the fact that the grains in these polycrystalline films have dimensions of only a few nm. Additionally, the low thickness of the films (typically 15 nm, as determined by spectroscopic ellipsometry) may play a role. For the PLD-grown samples, film thicknesses were typically between 300 and 500 nm.

### 3.2. Electrical Properties

The electrical conductivity of the studied samples was determined by four-point probe measurements. The values are listed in Table 2. Even though the single crystal is fully opaque, it has the second lowest conductivity of all the samples. For the sputtered films, it can be noted that the conductivity decreases with increasing oxygen partial pressure during deposition, in contrast to the typically observed behavior (higher $p_{O_2}$ causes lower formation energy for $V_{Ni}$ acceptor defects). This is likely caused by target poisoning, i.e., a high oxygen supply has led to an oxidation of the metallic Ni target surface before target ablation. The composition of the resulting film is closer to stoichiometry for higher $p_{O_2}$ than for a lower one.

To determine the carrier type, the hot-probe technique was used. p-type conductivity was found on all samples except the undoped thin film on MgO, where no thermovoltage could be detected.

### 3.3. Optical Absorption

In Figure 3, the imaginary component $\varepsilon_2$ of the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is shown for an undoped, epitaxial NiO thin film grown on MgO substrate. The absorption edge is well visible around 4 eV where $\varepsilon_2$ reaches a maximum. Reference data from ref. [28] are also shown, exhibiting the same features. The origin of the transitions observed in the range 4–7 eV has been ascribed to a series of $p$–$d$ charge transfer excitations.[29] The inset of Figure 3 shows the near-infrared and visible spectral range where $\varepsilon_2$ is slowly increasing, with some weak but visible features superimposed that have first been described by Reinen[30] and assigned to internal optical transitions on Ni$^{2+}$ ions—$d$–$d$ transitions that are forbidden by selection rules, but obtain nonzero transition matrix elements from disorder, mostly by defects and phonons. These lines are centered mainly in the red and blue ranges, and therefore can give otherwise optically clean samples a light-green hue. The reference data from ref. [28] do not contain these lines, likely because a total reflectance measurement was used which may not be sensitive enough to detect the weak electronic transitions on the Ni$^{2+}$ ions.

### Table 2. Electrical conductivity $\sigma$ of the samples under study.

| Sample         | Epitaxial Undoped | Li-doped | Single crystal | Sputtered [\text{p}_{O_2}, \text{mbar}^{-1}] |
|----------------|-------------------|----------|----------------|----------------------------------|
| $\sigma$ [Sm$^{-1}$] | $2.5 \times 10^{-3}$ | 500      | $2.4 \times 10^{-6}$ | 380                              |

We study next the induced changes of the optical absorption properties upon doping with Li and $V_{Ni}$. The imaginary part of the dielectric function $\varepsilon_2$ of a Li-doped and a $V_{Ni}$-doped (sputtered) NiO thin film is determined from numerical modeling of ellipsometry data, including a fit of this numerical dataset using a parameterized model (see Figure 4 and Supporting Information). The formation of two absorption bands is well documented for both doping methods, centered at approximately 1 and 2 eV for the Li-doped and 1.25 and 2.5 eV for the $V_{Ni}$-doped (here: $p_{O_2} = 1.75 \times 10^{-2}$ mbar) case, respectively. The parameterized model contains three Lorentz oscillators (two for the defect bands and one for the band-to-band transition at 4 eV) to reproduce the optical transitions in the near-IR and visible spectral ranges. Table 3 summarizes the parameter values for all three oscillators and the two dopant types.

For the Li-doped sample, which is visibly opaque, Figure 4 shows that the optical transmittance $T$ below 1 eV increases again, indicating that this sample resembles a narrow-bandgap material. This interpretation is also supported by the maximum value of $\varepsilon_2 \approx 6.5$ at 1 eV, which is almost as large as that at the original absorption edge in the undoped sample in Figure 3 ($\varepsilon_2 = 7.5$). Such high oscillator strengths of electronic transitions are usually found for band-to-band transitions. A similar transmission window for low photon energies is also seen in the single crystal (which was manually polished by SiC and diamond paper to increase the signal quality for the optical transmission measurement), also displayed in the top panel of Figure 4. This sample is shown to become transparent below...
photon energies of around 0.8 eV, indicating the existence of one or more absorption bands similar to the one observed for the doped thin films. The fact that the single crystal shows insulating behavior, in contrast to the Li-doped film, can be interpreted as evidence for hole compensation by donor states. These may originate from unknown impurities contained in the sample. Due to the roughness of the unpolished single crystal, ellipsometric measurements were not possible on this specimen. For the VNi-doped case, the absorption bands are shifted to higher photon energies, and are slightly broader than in the Li-doped sample. The doping-induced oscillator strengths are lower in this sample than in the Li-doped one, which corresponds to the difference in their electrical conductivity ($\sigma_{Li} = 500 \text{ S m}^{-1}$, $\sigma_{VNi} = 20 \text{ S m}^{-1}$).

Table 3. Parameters of the Lorentz oscillator model used for fitting the $\varepsilon_2$ spectra from Figure 4.

| Sample    | $\Delta_1$ | $\beta_1$ [eV] | $E_1^\prime$ [eV] | $\Delta_2$ | $\beta_2$ [eV] | $E_2^\prime$ [eV] | $\Delta_3$ | $\beta_3$ [eV] | $E_3^\prime$ [eV] |
|-----------|-------------|----------------|-------------------|-------------|----------------|------------------|-------------|----------------|------------------|
| Li-doped  | 5.04        | 1.86           | 1.18              | 0.69        | 0.75           | 2.12             | 2.63        | 3.26           | 3.56             |
| VNi-doped | 1.16        | 2.42           | 1.68              | 0.38        | 0.72           | 2.54             | 2.09        | 2.21           | 3.96             |

The two Li doping-induced absorption bands observed in this work have been described in the literature before.$^{[7,31,32]}$ The authors of ref. [7] suggest an energy scheme of the electronic states where Li doping leads to the formation of a set of broadened in-gap states approximately 1.1 eV above the VBM. The excitation from the VBM and a deeper-lying valence band likely related to O2p states into the Li acceptor band is assigned as the origin for the two absorption bands. This picture has been supported by experiments on Li-doped NiO probing the electronic structure of the material, such as X-ray absorption spectroscopy (XAS)$^{[31]}$ and electron energy loss spectroscopy (EELS).$^{[32]}$ Both methods show that upon Li incorporation, a new set of electronic states emerges approximately 1.2 eV above the valence band edge. A characteristic feature of the emergence of this band is spectral weight redistribution: the replacement of a magnetic Ni ion (single spin-degenerate state) by a nonmagnetic Li ion (double-degenerate state) creates the in-gap states at twice the rate by which conduction band states are being removed. This leads to a fast decrease of CB-related features. In Figure 5, O K-edge XAS spectra extracted from refs. [31,33] are shown, obtained on undoped, Li-doped, and VNi-doped material. The formation of the doping-induced band approximately 3 eV below the CBM-related feature at 532 eV is clearly visible in both cases. Simultaneously, the shape and intensity of the 532 eV peak change drastically because of spectral weight redistribution. It is interesting to note that the peak at 528 eV seen in

Figure 4. $\varepsilon_2$ data from Li-doped (top) and VNi-doped (bottom) NiO films obtained by numerical modeling of ellipsometry data, as well as from fitting by a parametrized model containing three Lorentz oscillators. The two absorption bands are highlighted in red. Dotted lines in top panel show increased optical transmittance for energies below approximately 1 eV for the Li-doped thin film and the single crystal. The VNi-doped sample was grown at a O2 partial pressure of $1.75 \times 10^{-2}$ mbar.

Figure 5. X-ray absorption spectra at the O K-edge of NiO for pure, Li-doped, and VNi-doped NiO. Data extracted from refs. [31,33]. Colored areas are spectral ranges exhibiting excitation from O 1s into defect-related (lighter red) and conduction band (darker red) states. The intensities have been normalized such that the curves coincide at their maxima at 540 eV.
doped samples is often claimed to be due to Ni$^{3+}$ states, such as in ref. [33], which refers to Kuiper et al.[31] Therein, however, it is stated that the large exchange interaction of the extra hole introduced by doping with the surrounding Ni$^{2+}$ spins only makes it appear as if there was Ni$^{3+}$ present. The authors conjecture that the 528 eV peak, in fact, originates from “impurity states in the gap, most likely bound to the effectively negative charged lithium sites,” and therefore support the defect interpretation. The Ni$^{3+}$ picture can be thought to describe the situation from the perspective of the intact Ni sublattice, whereas the defect picture describes the deviation from the perfect lattice periodicity. However, according to ref. [31], the idea of actual Ni$^{3+}$ ions lacks experimental support.

**Figure 6** shows optical reflectance $R$ and $\varepsilon_2$ spectra for four films grown by reactive magnetron sputtering at different oxygen partial pressures, which lead to varying VNi concentrations. To be able to interpret $R$ spectra without having to take into account interference fringes, the films were made very thin (between 10 and 12 nm). Here, one intense absorption band at photon energies 1.2–1.5 eV and a slight shoulder-like feature at 2.5 eV are seen to form, exhibiting increasing transition strength as the acceptor concentration increases. These features are visible both in the reflectance and the $\varepsilon_2$ data, which is to be expected as both quantities are directly related to the extinction coefficient, i.e., optical absorption. The inset of Figure 6 displays the relation between the electrical conductivity of the films and the value of $\varepsilon_2$ at 1.2 eV (as a measure of the magnitude of absorption), demonstrating that the increased optical absorption is correlated with higher [VNi]. Moreover, with increasing VNi concentration, the strength of the band-to-band transition as visible in the reflectance data at $\approx$ 4 eV (the fundamental bandgap) decreases, in accordance with the redistribution of spectra weight. The higher-order transition at approximately 5.5 eV is unaffected. Similar observations have been made by Egbo et al.[30] by spectroscopic ellipsometry on a VNi-doped NiO thin film. A broad absorption band appears with a maximum at around 1.5 eV, extending between 1 and 2.7 eV, accompanied by a reduction of the amplitude of $\varepsilon_2$ at the fundamental absorption edge at approximately 4 eV. We suggest to interpret these observations within the same framework that has already been applied to the case of Li-doped NiO. The introduction of Ni vacancies creates a defect level in the bandgap which can be populated by optical excitation of electrons from the valence band. With increasing doping, the concentration of this level becomes so high that the electronic transitions into it become similarly strong as the band-to-band-transitions of the undoped material. At the same time, the redistribution of the spectral weight from the conduction band into the defect band lowers the magnitude of $\varepsilon_2$ (and therefore also the reflectance) at the band-to-band transition energy of 4 eV. The higher-order transition is likely due to transitions into the O 3p band[31] which is not affected by the Ni deficiency to the same degree as the Ni 3d CBM. Egbo et al. have also studied the impact of other dopants in NiO (Cu, Ag, besides Li and VNi) on the optical and electrical properties[38] and found the appearance of broad absorption bands in the range 1–2.5 eV in all cases, with small but noticeable difference between the dopant species.

Although the emergence of these in-gap states upon doping is well documented, a direct interpretation within a defect picture that can be applied coherently to various dopants has not been suggested until now. Ono et al.[34] believe the absorption in the visible range to be from the abovementioned internal $d$–$d$ transitions of the Ni$^{2+}$ ion that are forbidden in the perfect crystal but become allowed when defects distort the lattice. This seems questionable for several reasons: 1) the absorption bands are significantly lower in energy than the originally two strongest $d$–$d$ lines at 1.75 and 3.25 eV, 2) the significant broadening of the acceptor-induced features compared to the Ni$^{2+}$ lines points toward a band-related origin rather than a local phenomenon like intraionic excitation, 3) the doping-induced features develop independently of those associated with Ni$^{3+}$ transitions in the pure material, as demonstrated in ref. [35], and 4) the observed difference of absorption band energies between dopant species cannot be explained within this framework. Ghosh et al. have attributed optical absorption starting from 0.8 eV to electronic transitions from the VB into a low-lying Ni 4s CB. However, the fact that this absorption gradually vanishes at elevated temperatures of a few hundred K remains unexplained within this model. Intriguingly, it agrees well with previous studies on the thermal instability of high concentrations of intrinsic defects (namely, VNi) in NiO[36,37]: elevated temperatures mobilize the VNi defects that ultimately reach the film surface where they disappear. This supports the attribution of the absorption band directly to the defect population.

### 3.4. Light Emission

**Figure 7a** displays a PL spectrum collected on the (100) surface of a NiO single crystal at 10 K using a 325 nm (3.81 eV) laser as excitation. In the visible spectral range, the PL intensity is generally low, and characterized by a broad emission band in the spectral range 2.0–3.3 eV, typically peaking at 2.2–2.4 eV. Under 5.03 eV excitation (Figure 7b), a narrow and intense
multicomponent feature appears between 3.24 and 3.33 eV. The emission properties of NiO have been studied previously in a few studies\cite{29,38–40} reporting on the same spectral features. Sokolov et al.\cite{29} have constructed a comprehensive scheme which explains the absorption and emission properties of the perfect NiO lattice by identifying three types of electronic transitions: 1) $p$–$d$ charge transfer (CT), 2) $d$–$d$ ($\text{Ni}^{2+}$) crystal field, and 3) $d$–$d$ charge transfer transitions. While type (1) and (2) only occur when exciting above the “charge transfer gap” of around 4 eV, the internal $\text{Ni}^{2+}$ transitions (2) occur preferably under sub-bandgap excitation, such as demonstrated in ref. \cite{39}. Sokolov et al. include in their model the possibility of a relaxation of the $p$–$d$ CT excitons into the localized excited states of type (2), thereby giving an explanation of the occurrence of emission in the visible spectral range when exciting with above-bandgap light. It is, however, interesting to note that when the authors use extreme UV light ($E_{\text{exc}} = 130$ eV) for excitation, which predominantly excites the bulk material and suppresses emission from defect-rich surfaces, these emission bands disappear completely. A correlation with defects therefore appears likely. The Sokolov model does not explicitly take radiative recombination through electronic defect states into account.

According to ref. \cite{29}, the $d$–$d$ CT excitons (3) recombine radiatively from a narrow-spaced state doublet into the ground state, emitting at energies close to 3.3 eV ($I_1$ and $I_2$ lines). A more recent work by Ho et al.\cite{40} studied the emission properties NiO nanostructures of high crystalline quality under 4.66 eV excitation for temperatures between 10 K and room temperature. It is claimed that the lines close to 3.3 eV can be resolved into a rich substructure which originates from different bound exciton complexes as well as donor–acceptor pair transitions. The 2.2–3.0 eV band is entirely absent in their study. Taking into account the high crystalline quality of the samples studied by Ho et al., a correlation of the occurrence of this band with defects appears convincing.

In Figure 7b, both the intensity of the green band and of the near-band edge emission (NBE) are shown to vary between the single crystal, the undoped, and the Li-doped thin films. While the absolute measured intensity can depend on various sample properties such as surface roughness or absorption coefficient, the ratio between the (defect-related) green band and the NBE is mainly affected by defect concentrations. Lower defect densities lead to longer exciton lifetimes because of decreased nonradiative recombination rates, which, in turn, increases NBE luminescence. Therefore, we suggest to assign the 2.2–3.0 eV band to radiative carrier recombination via defect states, while the 3.3 eV multiplet is caused by the recombination of excitons bound to defects.

### 3.5. Hybrid Functional Calculations

Figure 8 shows the formation energy of $\text{Li}_{\text{Ni}}$ and $\text{V}_{\text{Ni}}$, under O- and Ni-rich conditions, as a function of the Fermi-level position in the bandgap. $\text{Li}_{\text{Ni}}$ and $\text{V}_{\text{Ni}}$ act as single and double acceptors, respectively, and exhibit very low formation energies. This is consistent with the high solubility of Li in NiO and the observed p-type conductivity in samples grown under O-rich conditions or doped with Li. Previous calculations based on hybrid and semilocal functionals also indicate that the concentration of the potential hole killer $\text{V}_O$ will be low due to a high formation energy.\cite{5,41} The predicted (0/−) levels of $\text{Li}_{\text{Ni}}$ and $\text{V}_{\text{Ni}}$ occur at

\[ (0/−): E_{V_{\text{Ni}}} = 0.77 \text{ eV} \]
\[ (−2/−): E_{V_{\text{Ni}}} = 1.05 \text{ eV} \]
0.57 and 0.77 eV, respectively, and are both approximately 0.36 eV deeper than those obtained experimentally by means of thermal admittance spectroscopy (TAS) measurements on samples grown to be rich in \( \text{LiNi} \) and \( \text{VNi} \), respectively (0.19 and 0.41 eV, assigned to the \((0/–)\) levels\(^{[10]}\)). It should be noted, however, that the calculated levels represent the dilute limit (isolated defects). At high concentrations, the interaction between defects can lead to the formation of defect bands. In the case of \( \text{Li} \), the effects of alloying on the electronic and crystal structure are also not included in our calculations. The relative positions of the calculated \((0/–)\) levels of \( \text{LiNi} \) and \( \text{VNi} \) (energy separation of 0.20 eV), however, are in good agreement with the experimental data (0.22 eV difference\(^{[10]}\)). The present calculations also show that by introducing local lattice distortions (the so-called hole self-trapping energy, \( E_{\text{ST}} \)) is given by the total energy difference between a localized hole (including the cost of the local lattice distortion) and a delocalized hole in the perfect lattice.\(^{[23,42]}\) The calculated \( E_{\text{ST}} \) is 0.05 eV.

To investigate the optical transition energies of the \( \text{LiNi} \) and \( \text{VNi} \) acceptors, 1D configuration coordinate (CC) diagrams as schematically shown in Figure 9a were constructed. As ground and excited states, we take into account different charge states of the \( \text{LiNi} \) and \( \text{VNi} \) defects, alongside with VB holes or CB electrons where applicable. The resulting parameter values are collected in Table 4. We start by considering the optical transition of an electron from the VBM to the empty polaronic hole states of \( \text{LiNi} \) and \( \text{VNi} \). For \( \text{LiNi} \), which has only one acceptor level, the only possible transition is \( \text{LiNi}^+ + h^+ \rightarrow \text{LiNi}^+ + h^+ \text{VBM} \). This results in an absorption energy \( E_{\text{abs}} \) of 1.48 eV. For \( \text{VNi} \), there are two transitions: 1) \( \text{VNi}^+ + h^+ \rightarrow \text{VNi}^+ + h^+ \text{VBM} \) and 2) \( \text{VNi}^+ + h^+ \rightarrow \text{VNi}^+ + h^+ \text{VBM} \). Here, the first transition is associated with an absorption energy of 1.51 eV, which is close to the value obtained for the corresponding transition of \( \text{LiNi} \). The second transition yields a higher absorption energy of 1.88 eV.

Table 4. Parameter values determined from the configuration coordinate diagrams for different electronic states associated with defects: absorption, emission, and zero-phonon line energies \( E_{\text{abs}}, E_{\text{em}}, E_{\text{ZPL}} \) (all in eV), and change in configuration coordinate \( \Delta Q \) (in \( \text{amu}^{1/2} \text{ Å} \)). Important absorption and emission energies to be compared with experiment are highlighted in boldface font.

![Figure 9. Schematic 1D CC diagram, demonstrating the transitions between ground and excited states of an idealized electronic state, with absorption, emission, and zero-phonon line energies \( E_{\text{abs}}, E_{\text{em}}, E_{\text{ZPL}} \), and the CC displacement \( \Delta Q \).](image)

The strong polaronic distortion \( \Delta Q \approx 1.3 – 1.6 \text{ amu}^{1/2} \text{ Å} \) results in large relaxation energies (Franck-Condon shifts) in the 0.6–1 eV range (depending on the defect). Such strong electron–phonon coupling can be expected to result in significant vibrational broadening of the absorption onsets, in line with experimental data.\(^{[7,43]}\) In this case, the calculated absorption energies of the order of 1.48 and 1.5–1.8 eV for \( \text{LiNi} \) and \( \text{VNi} \), respectively, reproduces the experimental observations well. Note that the present calculations only consider transitions from the VBM to the polaronic hole states, i.e., transitions of electrons from lower-lying VB states are not included.\(^{[21]}\)

The radiative recombination of an electron in the CBM with a free or acceptor-bound small hole polaron, which reflects the situation in a PL experiment with above-bandgap light, leads to emission of a photon of energy \( E_{\text{em}} \). In order to excite acceptors to a state with a free electron in the CB, photon energies of between 3.94 and 4.61 eV are predicted to be required. Emission energies are calculated to be in the range 2–3.5 eV. The \((0/–)\) transitions of \( \text{LiNi} \) and \( \text{VNi} \) yield very close emission energies of 2.81 and 2.79 eV, respectively, while the \((–/2–)\) transition of \( \text{VNi} \) results in a lower emission energy of 2.42 eV. Considering the low formation energy of \( \text{VNi} \), this defect is a good candidate for the observed visible luminescence at the low energy side of the broad emission. For the small hole polaron (or self-trapped hole), the calculated emission energy is 3.28 eV, which is consistent with the 3.2 eV band observed here and in the literature and its assignment by Sokolov et al.\(^{[29]}\) For the process of generating the small polaron-free electron pair, above-bandgap excitation energies are necessary, explaining why the 3.2 eV multiplet appeared much more strongly when exciting above 5 eV.

4. Conclusion

By comparing experimental results with density functional theory (DFT) calculations, it could be shown that the optical absorption and light emission properties of NiO are dominated by defects present in the sample. Specifically, this work quantitatively describes the strong anticorrelation of electrical conductivity and optical transmittance of doped NiO, which has long been
known but lacked an explanation of its origin. Even though the main acceptors, such as Li$_{Ni}$ and V$_{Ni}$, possess fairly shallow electronic states that can be at least partially ionized at room temperature, the strong electron–phonon interaction leads to a significant blueshift of the optical transitions between different defect charge states. This renders heavily doped NiO essentially a narrow-gap semiconductor, with bandgap values of slightly above 1 eV. The results of the calculations are additionally tested by comparing the predicted light emission to experimental data, and excellent agreement has been found.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was funded by Sächsische Aufbaubank (SAB, project no. 100112104), Deutsche Forschungsgemeinschaft (DFG) in the framework of the collaborative research center “SFB 762: Functionality of Oxidic Interfaces” (project no. 31047526), and the Research Council of Norway (FUNDAMeNT, project no. 251131, NoSiCaR, project no. 257639). The computations were performed on resources provided by UNINETT Sigma2, the National Infrastructure for High Performance Computing and Data Storage in Norway. The Research Council of Norway is acknowledged for the support to the Norwegian Micro- and Nano-Fabrication Facility, NorFab (project no. 295864).

**Conflict of Interest**

The authors have no conflict of interest to declare.

**Data Availability Statement**

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

**Keywords**

devices, density functional theory (DFT) calculations, doping, nickel oxide, optical properties

---

[1] L. Xu, X. Chen, J. Jin, W. Liu, B. Dong, X. Bai, H. Song, P. Reiss, *Nano Energy* 2019, 63, 103860.
[2] R. Li, P. Wang, B. Chen, X. Cui, Y. Ding, Y. Li, D. Zhang, Y. Zhao, X. Zhang, *ACS Energy Lett.* 2019, 5, 79.
[3] M. Feng, M. Wang, H. Zhou, W. Li, S. Wang, Z. Zang, S. Chen, *ACS Appl. Mater. Interfaces* 2020, 12, 50684.
[4] A. Bielański, J. Dereń, J. Haber, J. Sloczyński, *Trans. Faraday Soc.* 1962, 58, 166.
[5] S. Lany, J. Osorio-Guillén, A. Zunger, *Phys. Rev. B* 2007, 75, 241203(R).
[6] M. Yang, H. Pu, Q. Zhou, Q. Zhang, *Thin Solid Films* 2012, 520, 5884.
[7] J. Y. Zhang, W. W. Li, R. L. Z. Hoye, J. L. MacManus-Driscoll, M. Budde, O. Bierwagen, L. Wang, Y. Du, M. J. Wahila, L. F. J. Piper, T.-L. Lee, H. J. Edwards, V. R. Dhanak, K. H. L. Zhang, *J. Mater. Chem. C* 2018, 6, 2275.
[8] K. O. Egbo, C. E. Ekuma, C. P. Liu, K. M. Yu, *Phys. Rev. Mater.* 2020, 4, 104603.
[9] K. O. Egbo, C. P. Liu, C. E. Ekuma, K. M. Yu, *J. Appl. Phys.* 2020, 128, 135705.
[10] R. Karsthof, H. von Wenckstern, V. S. Olsen, M. Grundmann, *AIP Mater.* 2020, 8, 121106.
[11] P. E. Blöchl, *Phys. Rev. B* 1994, 50, 17953.
[12] G. Kresse, D. Joubert, *Phys. Rev. B* 1999, 59, 1758.
[13] G. Kresse, J. Furthmüller, *Phys. Rev. B* 1996, 54, 11169.
[14] P. Liu, C. Franchini, M. Marsman, G. Kresse, *J. Phys.: Condens. Matter* 2019, 32, 015502.
[15] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, G. E. Scuseria, *J. Chem. Phys.* 2006, 125, 224106.
[16] C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, C. G. V. de Walle, *Rev. Mod. Phys.* 2014, 86, 253.
[17] C. Freysoldt, J. Neugebauer, C. G. V. de Walle, *Phys. Rev. Lett.* 2009, 102, 016402.
[18] Y. Kumagai, F. Oba, *Phys. Rev. B* 2014, 89, 195205.
[19] T. Gake, Y. Kumagai, C. Freysoldt, F. Oba, *Phys. Rev. B* 2010, 101, 020102(R).
[20] P. J. Gielisse, J. N. Plendl, L. C. Mansur, R. Marshall, S. S. Mitra, R. Mykolajewycz, A. Smakula, *J. Appl. Phys.* 1965, 36, 2446.
[21] A. Alkauskas, J. L. Lyons, D. Steiauf, C. G. V. de Walle, *J. Appl. Phys.* 2016, 119, 181101.
[22] A. Alkauskas, M. D. McCluskey, C. G. V. de Walle, *J. Appl. Phys.* 2012, 109, 267401.
[23] A. Alkauskas, K. O. Egbo, M. D. McCluskey, C. G. V. de Walle, *J. Appl. Phys.* 2016, 119, 174507.
[24] J. B. Varley, A. Janotti, C. Franchini, C. G. V. de Walle, *Phys. Rev. B* 2012, 85, 081109.
[25] M. Carey, F. Spada, A. Berkowitz, W. Cao, G. Thomas, *J. Mater. Res.* 1991, 6, 2680.
[26] E. Z. Kurmaev, R. G. Wilks, A. Moewes, L. D. Finkelstein, S. N. Shamin, J. Kuneš, *Phys. Rev. B* 2008, 77, 155127.
[27] G. A. Sawatzky, J. W. Allen, *Phys. Rev. Lett.* 1984, 53, 2339.
[28] T. Dutta, P. Gupta, A. Gupta, J. Narayan, *J. Appl. Phys.* 2010, 108, 083715.
[29] R. J. Powell, W. E. Spicer, *Phys. Rev. B* 1970, 2, 2182.
[30] V. I. Sokolov, V. A. Pustovarov, V. N. Churmanov, V. Y. Ivanov, N. B. Gruzdev, P. S. Sokolov, A. N. Baranov, A. S. Moskvin, *Phys. Rev. B* 2012, 86, 115128.
[31] D. Reinen, *Ber. Bunsenges. Phys. Chem.* 1965, 69, 82.
[32] P. Kuiper, G. Kruizinga, J. Chijisen, G. A. Sawatzky, H. Verweij, *Phys. Rev. Lett.* 1989, 62, 221.
[33] F. Reinert, P. Steiner, S. Hübner, H. Schmitt, J. Fink, M. Knupfer, P. Sandl, E. Bertel, *Z. Phys. B: Condens. Matter* 1995, 97, 83.
[34] R. J. O. Moshanek, G. Domnguez-Canizares, A. Gutiérrez, M. Abbate, D. Daz-Fernández, L. Soriano, *J. Phys.: Condens. Matter* 2013, 25, 495506.
[35] M. Ono, K. Sasaki, H. Nagai, T. Yamaguchi, M. Higashiwaki, A. Kuramata, S. Yamakoshi, M. Sato, T. Honda, T. Onuma, *Phys. Status Solidi B* 2018, 255, 1700311.
[36] G. Allen, J. Dyke, *Chem. Phys. Lett.* 1976, 37, 391.
[37] R. Karsthoef, M. A. Anton, F. Kremer, M. Grundmann, *Phys. Rev. Mater.* 2020, 4, 034601.
[38] A. Gutiérrez, G. Domnguez-Canizares, S. Krause, D. Daz-Fernández, L. Soriano, *J. Vac. Sci. Technol., A* 2020, 38, 033209.
[39] C. Díaz-Guerra, A. Remón, J. A. García, J. Piqueras, *Phys. Status Solidi A* 1997, 163, 497.
[39] V. V. Volkov, Z. Wang, B. Zou, *Chem. Phys. Lett.* **2001**, *337*, 117.
[40] C.-H. Ho, Y.-M. Kuo, C.-H. Chan, Y.-R. Ma, *Sci. Rep.* **2015**, *5*, 15856.
[41] J. A. Dawson, Y. Guo, J. Robertson, *Appl. Phys. Lett.* **2015**, *107*, 122110.
[42] J. B. Varley, J. R. Weber, A. Janotti, C. G. V. de Walle, *Appl. Phys. Lett.* **2010**, *97*, 142106.
[43] Y. K. Frodason, K. M. Johansen, A. Galeckas, L. Vines, *Phys. Rev. B* **2019**, *100*, 184102.