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The local atomic structure and thermoelectric properties of Ir-doped ZnO: hybrid DFT calculations and XAS experiments†

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We combined the hybrid density functional theory (DFT) calculations and X-ray absorption spectroscopy (XAS) experiments in the study of the local atomic structure around Ir ions in ZnO thin films with different iridium content. This was then used in the first principles analysis of the thermoelectric properties of material. The emphasis has been put on the conditions for a positive Seebeck coefficient and p-type electrical conductivity as the functions of the Fermi level. We studied both computationally and experimentally several possible IrO_x polyhedra (complexes) with a different number of surrounding oxygens and Ir oxidation states, including those with the formation of peroxide ions (O₂²⁻). In particular, octahedral coordination of iridium ions was identified by reverse Monte Carlo (RMC) simulations of the Ir L₃-edge EXAFS spectra of ZnO:Ir thin films as the predominant complex, which is supported by the calculated lowest interstitial oxygen incorporation energies. All the calculated IrO_x (x = 4, 5, 6) complexes, regardless of Ir the oxidation state, demonstrate potential for p-type conduction if the Fermi level (μ_F) falls in the range of 0–0.8 eV from the valence band maximum (VBM) and the Ir concentration is high enough (12.5% in the present DFT calculations). Even though the corresponding calculated Seebeck coefficient (S) around 80–89 $\mu\text{V K}^{-1}$ slightly exceeds the experimental values, we emphasise the presence of an important plateau in the dependence of S on μ_F in this range for two complexes with the formation of peroxide ions (O₂²⁻). We predicted also that peroxide ions O₂²⁻ are characterized by the calculated phonon frequencies of 810–942 cm^{-1} in agreement with our previous Raman experimental results. In this light, we discuss the high sensitivity of calculated S(μ_F) dependences to the atomic and electronic structure.

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Introduction

Zinc oxide (ZnO) is widely used in semiconductor and optoelectronic industries. Despite more than two decades of intensive research, the capabilities of ZnO are still not exhausted. It can be grown as large bulk single crystals of high quality,

deposited as thin films, or made amorphous.^{1–3} It has a 3.4 eV wide band gap, strong luminescence, high electron mobility, high thermal conductivity and large exciton binding energy. Due to these properties, ZnO is regarded as a promising material for a wide variety of applications, including but not limited to transparent conductors, sensors/emitters of blue and UV light, and to functional coatings.^{4,5} In particular, modern electronics requires stable p-type thin films with sufficiently high transparency and p-type conductivity. Modified ZnO can be a stable n-type conductor, and the current research focuses on achieving stable p-type conductivity. Concurrently, as a result of advances in growing methods, the research scope is also shifting towards an amorphous phase of ZnO.⁶

To date, there has been room for more details on a study of the behaviour of intrinsic and impurity defects in ZnO. A comprehensive analysis of intrinsic defect behaviour by using advanced optical measurements was recently performed for defect-rich single ZnO⁷ crystals. In the interpretation of

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photo-luminescence spectra the oxygen vacancies (V_O), the vacancy pairs (V_O-V_{Zn}), Zn interstitials and their complexes were identified. In ZnO electronic donors are formed spontaneously leading to intrinsic doping asymmetry.⁸ Even though the oxygen vacancy possesses the lowest formation energy under Zn and O-rich conditions in most theoretical studies on bulk material, understanding conditions for the growth of the thin films plays a very important role. The literature indicates that the analysis of defects in thin films should be done with caution. For instance, the Mn-doped ZnO thin films required theoretical computations to explain discrepancies in the interpretation of XANES (X-ray absorption near edge structure) spectra.⁹ It was established that neither O nor Zn vacancies are detectable in the XANES spectra. Their presence is less important than local structure changes induced by the Mn impurity. The present study focuses on the d-electron impurity, Ir. ZnO:cIr thin films (c is the Ir concentration) have demonstrated the change in the sign of the Seebeck coefficient from negative to positive for Ir concentration ranging from $c = 12.4$ to 16.4%.¹⁰ High oxygen partial pressure during the ZnO:cIr thin film deposition and film transformation into the amorphous phase with the Ir concentration $c = 7$ –16% at room temperature allows us to suggest an important role of oxygen interstitials (O_i 's).¹⁰ However, atomistic understanding of the changes in the ZnO:cIr thin film properties was missing. Notice that the present experiments considered a wider range of Ir concentrations and were mainly focused on the local atomic structure around Ir. Raman spectroscopy results revealed¹⁰ the existence of a vibrational band at 720 cm^{-1} , and it was argued that its presence is not due to the IrO_2 phase but is rather related to the formation of a peroxide moiety (O_2^{2-}). The existing body of work⁵ relating to ZnO largely agrees on the fact that O_i tends to form an O–O 'dumbbell' or 'split interstitial'. This may show both donor- and acceptor-like qualities as discussed based on DFT calculations.¹¹

Notice that previous DFT calculations of Ir-doped ZnO did not discuss the thermoelectric properties and the effect of Seebeck coefficient sign change.^{12–14} Thus, the present DFT calculations address these peculiar properties of ZnO:Ir thin films and explore the connection between the role of Ir impurity and O_i for the electronic structure, thermoelectrical properties and p-type conduction. We use several models of IrO_x polyhedra (called, hereafter, IrO_x complexes) in ZnO, distinguished by the number of oxygens surrounding Ir, the oxidation state of Ir, incorporation energy of O_i 's and the presence of peroxide defects. Thus, we can find interpretations in the Seebeck coefficient dependences on μ_F for potential p-type conduction in Ir-doped ZnO.

The experimental section describes details of preparing Ir-doped ZnO and pure IrO_x thin films and synchrotron radiation XAS measurements at the Ir L_3 -edge. Subsequent sections on methods introduce the models for the calculation of IrO_x complexes in ZnO and present computational details, including those regarding the thermoelectric properties. The results section is divided into several subsections to discuss the results of the extended X-ray absorption fine structure (EXAFS) spectra analysis

using reverse Monte Carlo (RMC) simulations, the calculated structural properties of IrO_x complexes in ZnO and those of the parent compounds, the electronic structure properties of IrO_x complexes in ZnO, and the main results of thermoelectric property calculations.

Methods

Experimental

Mixed zinc-iridium oxide (ZnO:cIr) and pure IrO_x amorphous thin films were deposited on polyimide tape substrates at room temperature by reactive DC magnetron co-sputtering in an Ar (20 sccm) + O_2 (10 sccm) atmosphere (10 mTorr working pressure). A metallic Zn (99.95 wt%) target with Ir (99.6 wt%) pieces placed on the target erosion zone were used for sputtering. The thin film thickness was about 200–300 nm. The iridium concentration ($c = 7\%$, 16%, 29%, 54% and 67%) was determined using X-ray fluorescence measurements. X-ray diffraction measurements confirm the amorphous structure of all films. More details about the experimental procedure can be found in ref. 10.

X-ray absorption spectra (XAS) at the Ir L_3 -edge were measured at room temperature at the SAMBA bending-magnet beamline¹⁵ of the Synchrotron SOLEIL storage ring. The experiments were performed in transmission mode using the focusing Si(220) monochromator and two ionization chambers. For each sample, a multi-layered sandwich was prepared to obtain a sufficiently large total thickness of samples with an absorption edge jump close to 1. The processing of XAS was performed using a conventional procedure,⁹ as implemented in the XAESA code.¹⁶

The Ir L_3 -edge EXAFS spectra in mixed zinc-iridium oxide (ZnO:cIr) and pure IrO_x thin films were analysed using the reverse Monte Carlo (RMC) method¹⁷ based on the evolutionary algorithm (EA), which is implemented in the EvAX code.¹⁸

DFT calculations

We have performed all DFT calculations using the Crystal17 v 1.0.2^{19–22} computer code. We used the supercell approach,²³ and as such we have modelled defective structures of ZnO (wurtzite structure with four atoms per unit cell, space group $P6_3mc$) using $2 \times 2 \times 1$ (*i.e.* four times extended unit cell L4, consisting of 16 atoms) or $4 \times 4 \times 3$ (L48, 192 atoms) supercells. These supercells represented 12.5 (L4) and 1.04 (L48) atomic % concentrations of Ir. In all cases, Ir ion substituted a regular Zn ion. In the following analysis, we refer to this defect as the Ir^nO_x complex, where n denotes the oxidation state²⁴ and x is the number of oxygen ions adjacent to Ir. In the wurtzite structure, Zn has four nearest O ions. Thus, we first model Ir surrounded by four host oxygen ions. In the results section we will show that $n = 2+$ in this case, *i.e.* Ir^{2+}O_4 . Other complexes included the O_i ions. In our calculations we considered numerous atomic configurations and used the incorporation energy of O_i 's (discussed below) to choose the most important ones. There is a different complex with four oxygen ions surrounding



Ir but with $n = 3+$, *i.e.* Ir^{3+}O_4 , due to only one O_i adjacent to Ir and simultaneously forming O_2^{2-} with a host oxygen (our first complex with the formation of O_2^{2-}). There is the complex with five oxygen ions surrounding Ir with $n = 4+$, *i.e.* Ir^{4+}O_5 , due to two O_i 's close to Ir. In this complex one of the O_i ions forms O_2^{2-} with the host oxygen (our second complex with the formation of O_2^{2-}). Lastly, there is the complex with six oxygen ions surrounding Ir with $n = 4+$, *i.e.* Ir^{4+}O_6 , due to two O_i 's close to Ir and without formation of O_2^{2-} . The atomic structure of each complex after the full structure relaxation can be seen in Fig. 5 and in Fig. S1 (ESI†).

We analyse the oxidation state n of Ir^nO_x in the different complexes by comparing it to reference materials: IrO_2 (formal oxidation state of iridium is 4+), a hypothetical Ir_2O_3 (formal oxidation state 3+), and to ZnIr_2O_4 (formal oxidation state 3+). All these materials were modelled in their common reported structures: tetragonal (space group $P4_2/mn$, rutile structure) for IrO_2 , rhombohedral (space group $R\bar{3}c$, corundum structure) for Ir_2O_3 , and cubic (space group $Fd\bar{3}m$, spinel structure) for ZnIr_2O_4 . To the best of our knowledge, the preparation of single-crystal Ir_2O_3 is not yet reported. However, its presence in IrO_2 powders was discussed in ref. 25 and 26, and corundum $\text{Ir}_2\text{O}_3(001)$ surface oxide was synthesized at high oxygen pressure²⁷ in the oxidation of the Ir(111) surface. Besides, several papers describe and report measurements of properties of devices based on corundum-structured Ir_2O_3 , although without discussing the actual structure of the material.^{28,29}

Our DFT calculations are based on the method of linear combination of atomic orbitals (LCAO). We use atom-centered basis sets (BS) of Gaussian-type functions adopted from the literature. The relativistic effective core pseudopotential with 60 core electrons³⁰ and basis set of triple-zeta valence with f-polarization function^{30,31} for Ir were taken from the Basis Set Exchange resource³² and used earlier by Ping *et al.*³³ All-electron BSs for O and Zn were taken from ref. 33 and Gryaznov *et al.*,³⁴ respectively. We modified the basis set for Zn by optimizing exponent values of the two most diffuse orbitals: one from the sp series and one from the d series (see the ESI† for details). We optimized these values with respect to the total electronic energy of the system with constant volume and atomic positions. The convergence limit of this procedure, based on the Powell's conjugate direction method and used as implemented in the OPTBAS³⁵ interface to CRYSTAL, was set to 10^{-5} a.u. For all other calculations, the convergence limit on the total energy for the self-consistent field procedure was set to 10^{-7} a.u. for both electronic and lattice structure relaxation.

As the exchange–correlation functional we chose a hybrid PBE0 functional with 25% of Hartree–Fock exchange.³⁶ We should mention that the bandgap value of pure ZnO obtained in the present calculations with the PBE0 functional is 3.45 eV, a value that is reasonably close to the experimental value of 3.44 eV³⁷ and which did not require an increase of the amount of exact exchange suggested in the literature for the HSE functional.³⁸ Indeed, our test calculation with the HSE

functional showed a band gap of 2.93 eV, suggesting that this effect is basis-independent. The Brillouin zone was sampled with either $4 \times 4 \times 4$ (for the L4 supercell) or a $2 \times 2 \times 2$ (L48) Γ -centered k -point mesh generated with the Monkhorst–Pack³⁹ method. All calculations of defective structures in the neutral supercells were spin-polarized and did not include the spin–orbit effects; the use of symmetry operations was explicitly omitted. Computational parameters (the choice of basis sets, functional and integration precision) have been validated to faithfully represent the bulk properties of ZnO , IrO_2 and Ir_2O_3 , and ZnIr_2O_4 .

O_i incorporation energy

As discussed above, the IrO_x complexes with n exceeding 2+ are not obtainable in the wurtzite structure by simply substituting Zn with Ir. The number of oxygen neighbours for each cation in the wurtzite structure is 4. Therefore, the additional O_i atoms are required. Thus, in our calculations for the Ir^{3+}O_4 , Ir^{4+}O_5 and Ir^{4+}O_6 complexes defective L4 supercells contain 18 ions (8 metals and 10 oxygens) meaning two O_i 's were added. The large supercell L48, containing 194 ions (96 metals and 98 oxygens) was used for the Ir^{4+}O_6 only. Optimization of atomic positions in a defective supercell may lead to very different atomic configurations; therefore, energetic criteria are important for their comparison. To compare systems of different atomic configurations we use the so-called incorporation energy, calculated from total electronic energies:

$$E_{\text{inc}}(\text{O}_i) = E(\text{O}_i) - E(\text{Ir}) - E(\text{O}_2), \quad (1)$$

where $E(\text{O}_i)$ is the total electronic energy of the supercell with two O_i atoms and with an Ir atom, $E(\text{Ir})$ is the total electronic energy of the supercell with Ir^{2+}O_4 and without O_i , and $E(\text{O}_2)$ is the total electronic energy of an oxygen molecule. The incorporation energies were successfully introduced to analyze the stability of fission products at different pre-existing trap sites in UO_2 .⁴⁰ Pre-existing trap sites may include vacancies and interstitials. In the case of interstitial sites, the incorporation energy coincides with the solution energies being different by the formation energy of the trap site. A negative value of incorporation energy means that incorporation is energetically favourable. All total electronic energies in eqn (1) are calculated using the same basis set and exchange–correlation functional. The results of $E_{\text{inc}}(\text{O}_i)$ as discussed below correspond to the concentration of Ir $c = 12.5\%$ (L4) only.

Calculation of thermoelectric properties

CRYSTAL17 allows post-process DFT wavefunctions for evaluating the electron transport properties by solving the Boltzmann equation. Unlike other approaches implemented in popular codes such as BoltzTrap⁴¹ or BoltzWann,⁴² CRYSTAL17 performs analytical derivatives of the electronic bands. Several studies have shown that all these codes, despite their differences, yield similar results.^{43,44} At the core of the equations for the transport coefficients (such as Seebeck coefficient and electronic conductivity) is the transport distribution function,



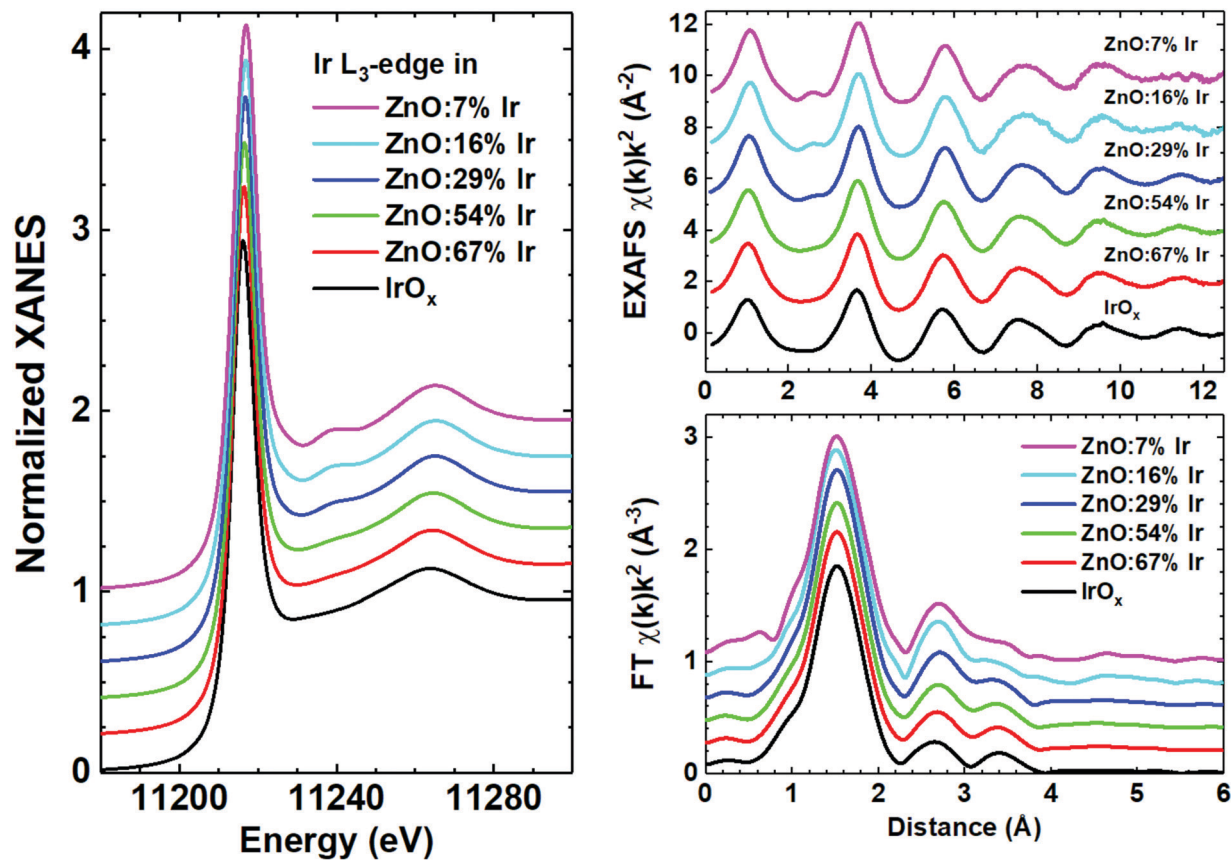


Fig. 1 Experimental Ir L_3 -edge XANES (left panel), EXAFS and their Fourier transforms (FT) (right panel) for mixed zinc-iridium oxide (ZnO:clr) and pure IrO_x thin films.

cast here as the energy projected tensor:

$$\Xi_{qr}(E) = \tau \sum_k \frac{1}{N_k} \frac{1}{V} \sum_{ij} v_{i,q}(k) v_{j,r}(k) \delta(E - E_i(k)), \quad (2)$$

where N is the number of k -points used in sampling the reciprocal space, $v_{i,q}(k)$ is the velocity of the i th (j th) band calculated along the direction q (r), δ is an approximation to Dirac's delta function, and τ is the electronic relaxation time which is assumed to be not dependent on k (constant relaxation time approximation). Relaxation time is temperature-dependent and cannot be obtained from first-principles calculations, and, therefore, must be either fitted or obtained experimentally.^{20,43} Throughout our calculations, we have used $\tau = 10$ fs, which is a conservative estimate for a system leaning towards conductivity. Values of τ for ZnO, calculated from mobility data found in the literature, range from 17 to 57.9 fs for carrier concentrations $ca. \sim 10^{16} \text{ cm}^{-3}$.^{45,46}

By integrating the conductivity distributions written with tensors of eqn (2), it is possible to obtain conductivity tensors, for instance, the electrical conductivity σ :

$$\sigma_{qr}(T; \mu) = e^2 \int dE \left(-\frac{\partial f_0}{\partial E} \right) \Xi_{qr}(E), \quad (3)$$

where μ is the chemical potential or Fermi level, E is the energy, f_0 is the Fermi-Dirac distribution, and T is the temperature.

Thermoelectric coefficient σS , where the Seebeck coefficient S is cast as:

$$[\sigma S]_{qr}(T; \mu) = \frac{e}{T} \int dE \left(-\frac{\partial f_0}{\partial E} \right) (E - \mu) \Xi_{qr}(E). \quad (4)$$

For convenience, we use the Fermi level $\mu_F = \mu - E_{\text{VBM}}$ for the analysis of the main results, where E_{VBM} is the valence band maximum. The transport coefficients were calculated in CRYSTAL with the Fermi level step (parameter to MURANGE) equal to 0.1 eV and the energy step (parameter to TDFRANGE) of 0.05 eV for the supercell L4 ($c = 12.50\%$). Notice that the same parameters should be chosen with caution for the supercell L48 ($c = 1.04\%$). Our careful treatment of these parameters for L48 suggested both the Fermi level step and the energy step should equal 0.05 eV.

Results and discussion

Structural properties of synthesized samples

Careful examination of the experimental EXAFS spectra and their FTs (Fig. 1) suggests that the local environment around iridium atoms is quite disordered, being typical for nanocrystalline or amorphous IrO_x films.⁴⁷ Indeed, reliable structural contributions are present in FTs up to about 4 Å and consist of three peaks: the main peak at 1.5 Å is due to the nearest oxygen atoms of the first



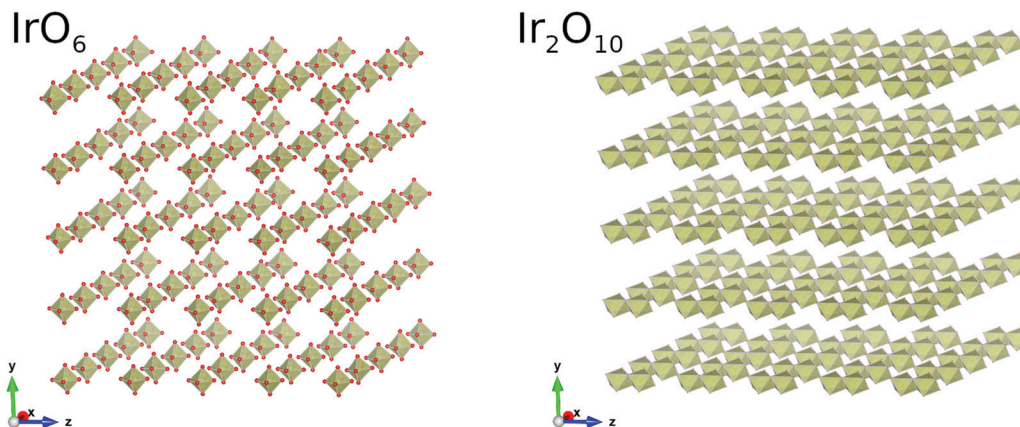


Fig. 2 Two $5 \times 5 \times 5$ supercell models used in the RMC simulations and composed of single IrO_6 octahedra (left) and groups of two IrO_6 octahedra joined by the edge (right).

coordination shell, while the origin of the next two peaks at 2.5 and 3.5 Å should be clarified. Our previous experience suggests that in metal oxide thin films such peaks can be due to multiple-scattering (MS) effects within the first coordination shell of the metal atom⁴⁸ with additional contributions originating from metal atoms located in the second coordination shell.⁴⁹ Thus, the structural model required to describe the local environment of iridium should be cluster-like, *i.e.* containing a few atoms. Besides, the closeness of the experimental Ir L_3 -edge XANES and EXAFS spectra for pure IrO_x and Ir-doped ZnO thin films gives strong evidence for the similarity of their structures. The Ir L_3 -edge XANES is dominated by the white line at $\sim 11\,217$ eV due to the dipole allowed transition $2p_{3/2}(\text{Ir}) \rightarrow 5d(\text{Ir}) + 2p(\text{O})$.⁵⁰ A decrease of the iridium concentration leads to the appearance of the shoulder at 11 240 eV, also visible in the EXAFS spectra at 2.5 \AA^{-1} ; it is due to the damped high-frequency contribution originating from peaks at 2–4 Å in FTs. Thus, all samples can be roughly divided into two groups, having close XANES and EXAFS spectra; the first group with $c \leq 29\%$ and the second group with $c \geq 54\%$ and pure IrO_x .

Crystalline IrO_2 adopts the rutile-type structure (space group $P4_2/mnm$) with slightly distorted ($2 \times 1.96 \text{ \AA}$ and $4 \times 2.00 \text{ \AA}$) octahedral coordination of iridium atoms by oxygens.⁵¹

The IrO_6 octahedra are joined by edges along the c -axis direction forming chains, which are cross-linked by shared corners to four neighbouring chains.⁵¹ Therefore, we used different fragments of the rutile IrO_2 structure to construct two structural models for RMC simulations. The first model included a single IrO_6 octahedron, whereas the second model contained two IrO_6 octahedra joined by the edge. In both cases, a $5 \times 5 \times 5$ supercell (a simulation box) was constructed (Fig. 2) and used in the RMC/EA simulations to get sufficient statistics from 125 independent structural units (IrO_6 or Ir_2O_{10}). Each iridium-oxygen unit was placed in the centre of the cell with a large enough size ($10 \text{ \AA} \times 10 \text{ \AA} \times 10 \text{ \AA}$) to exclude the influence of units located in the neighbouring cells on each other.

The details of the RMC/EA method were described previously.^{17,18} The number of simultaneously used atomic configurations in the EA method was 32. At each iteration,

the new atomic configuration was generated by randomly displacing all atoms in the simulation box with the maximally allowed shift of 0.4 Å to get the best possible agreement between the Morlet wavelet transforms (WTs) of the experimental and calculated EXAFS spectra $\chi(k)k^2$. The calculations were performed in the k -space range from 1.5 to 11 \AA^{-1} and in the R -space range from 0.8 to 4.0 Å. No significant improvement in the residual was observed after 5000 iterations.

The configuration-averaged EXAFS spectra during each RMC/EA simulation were calculated using *ab initio* real-space multiple-scattering (MS) FEFF8.50L code,^{52,53} including the MS effects up to the 4th order. The scattering potential and partial phase shifts were calculated for each absorption edge only once within the muffin-tin (MT) approximation^{52,53} for the cluster with a radius of 5 Å, constructed from the rutile IrO_2 structure and centred at the absorbing iridium atom. Small variations of the cluster potential due to atom displacements during the RMC/EA simulations were neglected. The complex exchange-correlation Hedin-Lundqvist potential was used to account for the photoelectron inelastic losses within the one-plasmon approximation.⁵⁴ The amplitude reduction factor S_0^2 was included in the scattering amplitude,^{52,53} calculated by the FEFF code, and no additional correction of the EXAFS amplitude was performed.

The results of the RMC/EA simulations for two selected samples from each group are reported in Fig. 3 and 4. As one can see, two simple structural models (Fig. 2) provide good agreement with the experimental data, reproducing contributions from all peaks observed in FTs. In ZnO:cIr samples with $c \leq 29\%$, iridium atoms are octahedrally coordinated by six oxygens with $R(\text{Ir-O}) = 1.93 \pm 0.02 \text{ \AA}$ and the mean square relative displacement (MSRD) $\sigma^2(\text{Ir-O}) = 0.0050 \pm 0.0005 \text{ \AA}^2$. The group of peaks located at longer distances in FT is solely due to the MS effects within the IrO_6 octahedron. In ZnO:cIr samples with $c \geq 54\%$ and pure IrO_x , iridium atoms are also octahedrally coordinated by six oxygens with slightly longer mean bonds $R(\text{Ir-O}) = 1.96 \pm 0.02 \text{ \AA}$, having slightly larger MSRD $\sigma^2(\text{Ir-O}) = 0.0065 \pm 0.0005 \text{ \AA}^2$. However, there is an additional iridium atom from the neighbouring octahedron located at $R(\text{Ir-Ir}) = 3.15 \pm 0.02 \text{ \AA}$ with



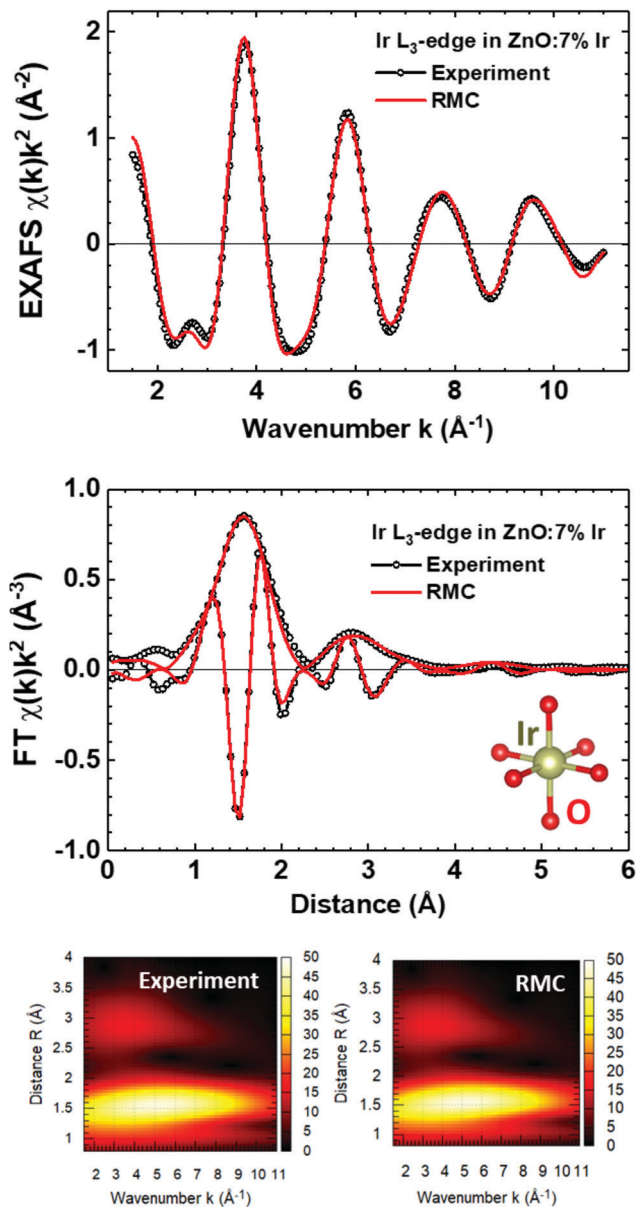


Fig. 3 Experimental and calculated by RMC Ir L_{3} -edge EXAFS spectra $\chi(k)k^2$ and their Fourier and Morlet wavelet transforms for the ZnO:7% Ir thin film.

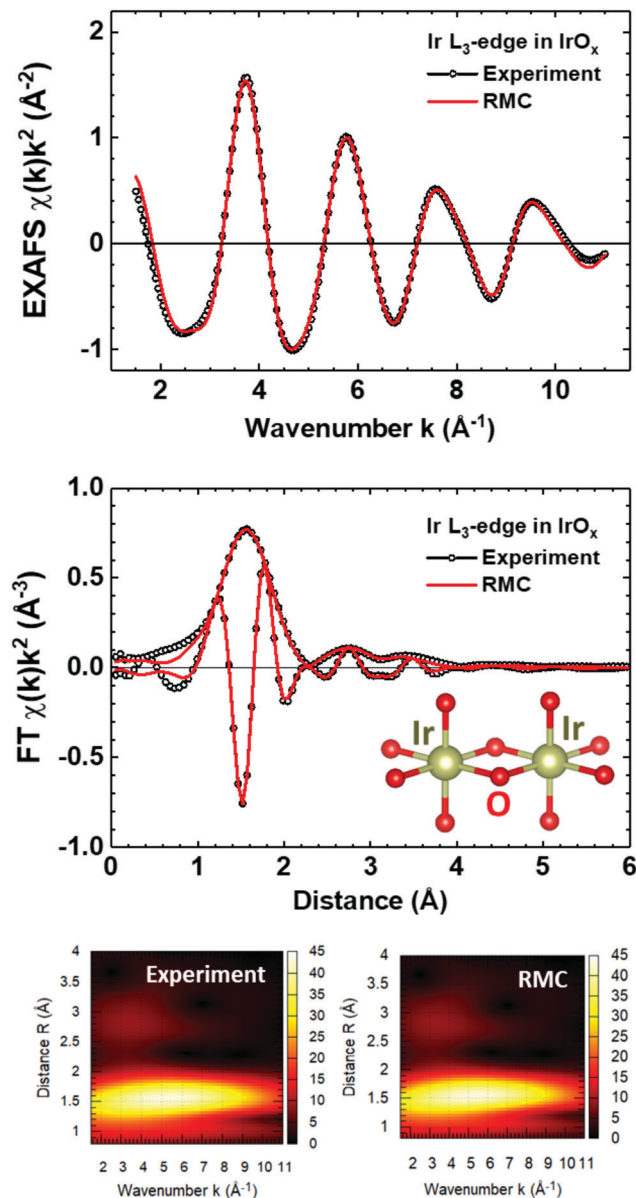


Fig. 4 Experimental and calculated by RMC Ir L_{3} -edge EXAFS spectra $\chi(k)k^2$ and their Fourier and Morlet wavelet transforms for the pure IrO_x thin film.

MSRD $\sigma^2(\text{Ir}-\text{Ir}) = 0.0056 \pm 0.0005 \text{ \AA}^2$, whose EXAFS, together with that from the remaining 4 oxygen atoms, interferes with the MS contribution from the first shell, resulting in the two-peak structure in FT. Thus, at high Ir dopant concentration and in pure IrO_x films, structural groups of two IrO_6 octahedra joined by the edge can be evidenced. These groups form chains in crystalline rutile-type IrO_2 .⁵¹

DFT atomic structures of iridium–oxygen complexes in ZnO and parent compounds

We focus our discussion of the oxidation state n of Ir in the Ir^nO_x complex in ZnO on an analogy with “pure” reference compounds: IrO_2 , Ir_2O_3 , and ZnIr_2O_4 (see the computational

details in Methods section). In either structure, Ir is six-fold coordinated, and in both IrO_2 and Ir_2O_3 the six neighbouring

Table 1 Calculated bulk properties of IrO_2 , Ir_2O_3 , and ZnIr_2O_4 . a and c are the lattice parameters, $d_{\text{Ir}-\text{O}}$ is the Ir–O interatomic distance, $q_{\text{Ir}}(\mu_{\text{Ir}})$ and $q_{\text{O}}(\mu_{\text{O}})$ are the effective atomic charges (magnetic moments) of Ir and O, respectively, and ΔE is the bandgap value. An extended table (Table S1, ESI) with experimental data for comparison is present in the ESI

Crystal	$d_{\text{Ir}-\text{O}}$, \AA	q_{Ir} , e	μ_{Ir} , μ_{B}	q_{O} , e	μ_{O} , μ_{B}	ΔE , eV
IrO_2	Short: 1.942	1.712	0.625	−0.856	0.171	Metal
	Long: 1.999					
Ir_2O_3	Short: 2.053	1.241	0.000	−0.827	0.000	3.39
	Long: 2.085					
ZnIr_2O_4	2.069	1.067	0.000	−0.824	0.000	3.44



oxygens are split into two groups (orbitals) by symmetry, yielding long (axial) and short (azimuthal) Ir–O distances. The calculated lattice parameters of IrO₂ and ZnIr₂O₄ are consistent with the experimental data (Table S1, ESI[†]). Our results show several possible ways to distinguish Ir³⁺ from Ir⁴⁺ (Table 1). First, the magnetic moment (μ_{Ir}) of Ir demonstrates that Ir in all these oxides is in the low-spin state with electron configurations 5d⁵ ($n = 4+$, IrO₂) and 5d⁶ ($n = 3+$, Ir₂O₃ and ZnIr₂O₄). Second, the effective atomic charge of Ir (q_{Ir}) is quite different for $n = 3+$ and $4+$, which makes it a useful descriptor for comparing different Ir^{*n*}O_{*x*} complexes. Thus, the larger (q_{Ir}) in IrO₂ than in Ir₂O₃ and ZnIr₂O₄ is in accordance with a larger n in the former. Third, the Ir–O distances are typically longer for Ir³⁺ than for Ir⁴⁺ as shown in Table 1.

The smaller ionic radius of Ir⁴⁺ leads to a smaller lattice constant in IrO₂ and, therefore, stronger hybridization between the Ir and O electronic states. Interestingly, the bandgap (ΔE) values in Ir₂O₃ and ZnIr₂O₄ are quite close. It was discussed earlier that the use of the hybrid exchange–correlation functional is critical to reproduce the bandgap in ZnIr₂O₄.¹³ The calculated ΔE for ZnIr₂O₄ in the present study is well comparable with the recently obtained experimental data in ref. 55.

In Tables 2 and 3 we present basic properties of the most important configurations of Ir^{*n*}O_{*x*} complexes, distinguished by the number of surrounding oxygens, incorporation energy (eqn (1)), oxidation state n , and formation of peroxide fragments (or lack thereof). The main difference between the configurations is due to the number of oxygens surrounding Ir. We, thus, obtain the configurations with the number of surrounding oxygens ranging from 4 to 6, whereas n varies from 2+ to 4+. The obtained n -values are consistent with the oxidation states analysis for amorphous IrO_{*x*} powders.⁵⁶ It was shown in that work that the average oxidation state of Ir is around 3.6 indicating the presence of Ir³⁺ and Ir⁴⁺ in the powders. The Ir oxidation state is 2+ if the interstitial oxygens are absent (Ir²⁺O₄). In this case, $d_{\text{Ir–O}}$, q_{Ir} and μ_{Ir} are obviously different from the other oxidation states and configurations in Table 2.

In the case of the Ir³⁺O₄ complex, Ir has four neighbors, too, and yet in this case the properties of Ir are not the same as in the Ir²⁺O₄ case. In Ir³⁺O₄, the value of μ_{Ir} corresponds to $n = 3+$ and an intermediate spin state (the formal value of $\mu_{\text{Ir}} = 2 \mu_{\text{B}}$). However, $d_{\text{Ir–O}}$ in the Ir³⁺O₄ complex differs from that in Ir₂O₃ and ZnIr₂O₄ (Table 1). It is smaller than in the parent oxides whereas q_{Ir} in Ir³⁺O₄ is close to the one of Ir in Ir₂O₃. The other two cases of Ir⁴⁺O₅ and Ir⁴⁺O₆ are characterized by small magnetic moments of Ir, consistent with the low spin

Table 3 Incorporation energy ($E_{\text{inc}}(\text{O}_i)$) of interstitial oxygens O_{*i*} (eqn (1)) in the different complexes (supercell L4, $c = 12.5\%$), $d_{\text{O–O}}$ is the O–O interatomic distance, and the local vibrational frequency (ν) of peroxide

Complex	Peroxide	$d_{\text{O–O}}$, Å	$E_{\text{inc}}(\text{O}_i)$, eV	ν , cm ^{−1}
Ir ³⁺ O ₄	Yes	1.47	−3.77	942
Ir ⁴⁺ O ₅	Yes	1.54	−4.37	810
Ir ⁴⁺ O ₆	No	—	−5.15	—

configuration of the 5d⁵ orbital. Such magnetic moments of Ir are very close to that in IrO₂ (Table 1). In contrast to other complexes, the O_{*i*} ions are Ir's nearest neighbors in the Ir⁴⁺O₆ complex, and do not participate in the formation of peroxide defects.

The Ir–O distances are shorter in the complexes containing the O_{*i*} ions than in the Ir²⁺O₄ case and parent compounds, which is connected with a greater overlap of the orbitals and results in an increased oxidation state of Ir. The calculated average Ir–O bond length of the Ir⁴⁺O₆ complex matches experimental data obtained with EXAFS (1.94 Å vs. 1.96 Å). Interestingly, the larger supercell (L48) used for the Ir⁴⁺O₆ complex did not demonstrate any changes in the basic properties (Table 1).

Table 3 indicates that the six-fold coordinated Ir is the energetically preferable state, as it is characterized by the lowest energy of incorporation. However, the Ir³⁺O₄ and Ir⁴⁺O₅ complexes contain the peroxide defects, formed by one O_{*i*} ion and one host oxygen ion. The interatomic distances ($d_{\text{O–O}}$) between these two oxygens are consistent with the values known for this type of defect (dumbbell) in other materials and ZnO from the DFT calculations.^{11,57–59}

From the experimental viewpoint, the O–O bond in O₂^{2−} has been reported to have a length varied from 1.47 to 1.54 Å for Ir(O₂) complexes in organic compounds.^{60–62} The stretching vibration of the O–O bond has been assigned⁶² an IR absorption band at $\nu = 833 \text{ cm}^{-1}$. Likewise, $d_{\text{O–O}}$ of 1.47 Å has been reported for a cubic zinc peroxide (ZnO₂).⁶³ In the latter study, authors have observed a strong Raman peak centred at 835 cm^{-1} , which they attribute to the O–O stretching vibration through comparison with other published data.^{64,65} However, a larger calculated $d_{\text{O–O}}$ equal to 1.75 Å for ZnO₂ was associated with the experimentally measured ν of 748 cm^{-1} taken from the literature (see ref. 66 and references therein). Importantly, the present calculated ν 's of peroxide defect are only slightly larger than the measured one of 720 cm^{-1} for Ir-doped ZnO.¹⁰

Analysis of the electronic structure

Even without O_{*i*}'s, Ir induces a non-zero spin on neighbouring oxygen ions in the Ir²⁺O₄ complex. The magnetic moment of its

Table 2 Basic properties of Ir^{*n*}O_{*x*} complexes. $d_{\text{Ir–O}}$ is the average Ir–O interatomic distance, q_{Ir} is the effective atomic charge of Ir, and μ_{Ir} is the magnetic moment of Ir. Two supercell sizes were used for the Ir⁴⁺O₆ complex for comparison, namely L4 and L48. Data obtained for the larger (L48) supercell is given in parentheses. Note that the Zn–O distance in ZnO is 1.98 Å

Complex	$d_{\text{Ir–O}}$, Å	$d_{\text{Ir–O}}$, Å (avg)	q_{Ir} , <i>e</i>	μ_{Ir} , μ_{B}
Ir ²⁺ O ₄	2.136–2.176	2.147	0.751	2.530
Ir ³⁺ O ₄	1.846–1.920	1.885	1.193	1.795
Ir ⁴⁺ O ₅	1.828–2.024	1.954	1.095	0.695
Ir ⁴⁺ O ₆	1.893–1.972 (1.892–2.047)	1.938 (1.936)	1.325 (1.366)	0.514 (0.507)



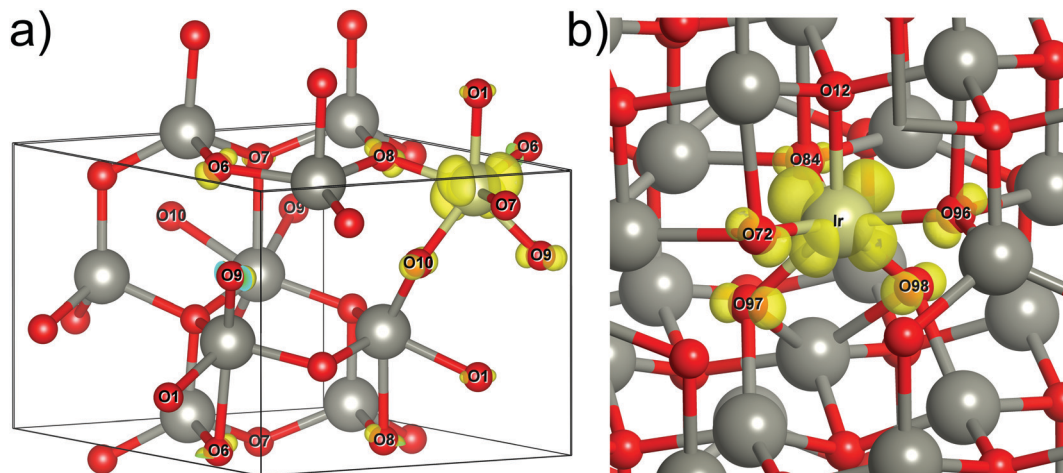


Fig. 5 The atomic structure and spin-density distribution in the small L4 (a) and large L48 (b) supercell for the Ir^{4+}O_6 complex. Light yellow spheres represent Ir atoms, gray – Zn, and red – O atoms. Yellow clouds represent orbitals with unpaired electrons. Teal clouds are the same orbitals sectioned by the periodic boundary. The box marks the supercell boundaries. All named oxygen atoms are bound to Ir and have a nonzero spin.

4 O neighbours varies from 0.10–0.12 μ_{B} . Such values of the magnetic moment are of the same order as those for the oxygens surrounding Ir in the complexes with O_i^{\cdot} 's. This is also well demonstrated by the spin density distribution shown in Fig. S1a–c (ESI[†]) and Fig. 5. The maximum spin density is localized on Ir whereas there is some part of the spin density on the nearest oxygen neighbours. A non-zero spin of oxygen ions surrounding Ir and the fact that these ions have a decreased charge (not shown) in comparison with other oxygen ions are very much in line with the same properties of IrO_2 in contrast to Ir_2O_3 and ZnIr_2O_4 (Table 1). Ir is fully oxidized, and the

electrons given to surrounding oxygens are distributed between them, including O_i^{\cdot} 's. This facilitates hole localization in Ir-doped ZnO. Interestingly, in the case of peroxide defect, the resultant fragment is asymmetric, with different magnetic moments of the two oxygens. Notice, however, that the magnetic moments of oxygens in O_2^{2-} are more pronounced in the Ir^{4+}O_5 complex than in the Ir^{3+}O_4 one due to the smaller O–O distance in the former case.

Analysis of the calculated density of states (DOS) for the Ir^{4+}O_6 complex (Fig. 6 and 7c) revealed that the top of the valence band consists of Ir states and states of oxygens

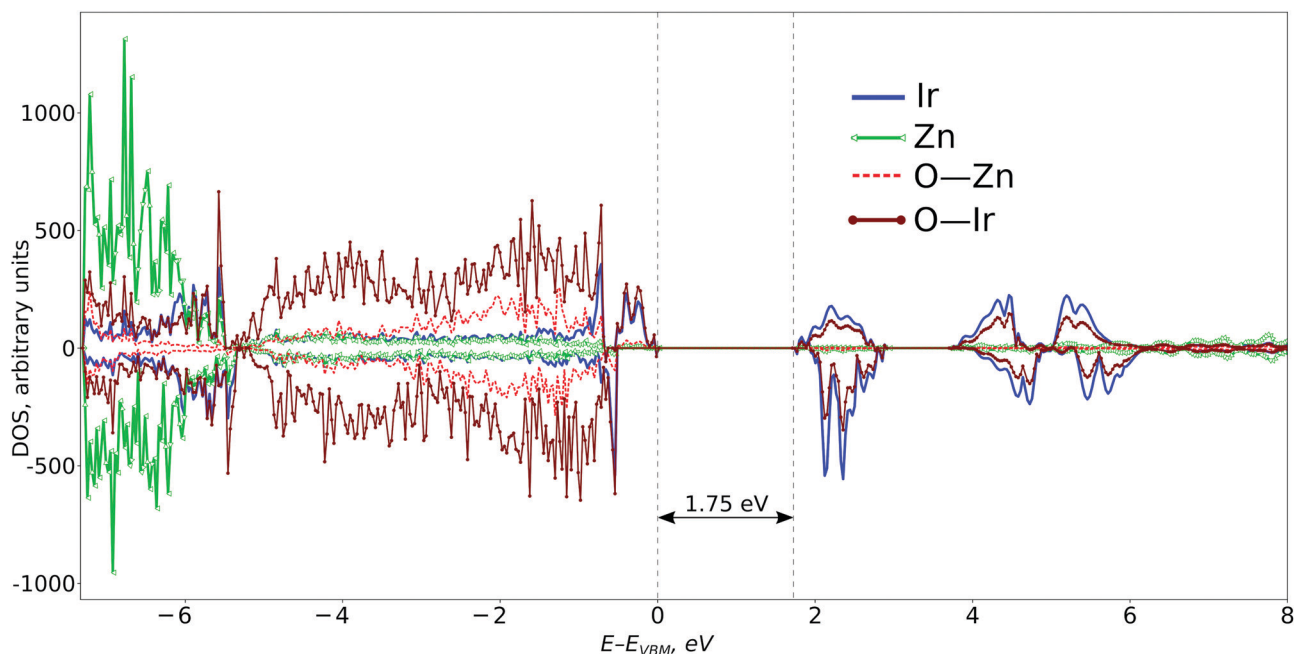


Fig. 6 Total and partial density of states (DOS) for Ir^{4+}O_6 calculated with the small supercell (L4). The O–Ir line describes the 6 oxygens surrounding Ir, whereas the O–Zn line is for all the other oxygens in the supercell. The valence band maximum (E_{VBM}) is taken as zero. Negative DOS values correspond to the spin-down electrons. Signals of Ir, O–Zn, and O–Ir are scaled by factors of 10, 3, and 5 respectively.



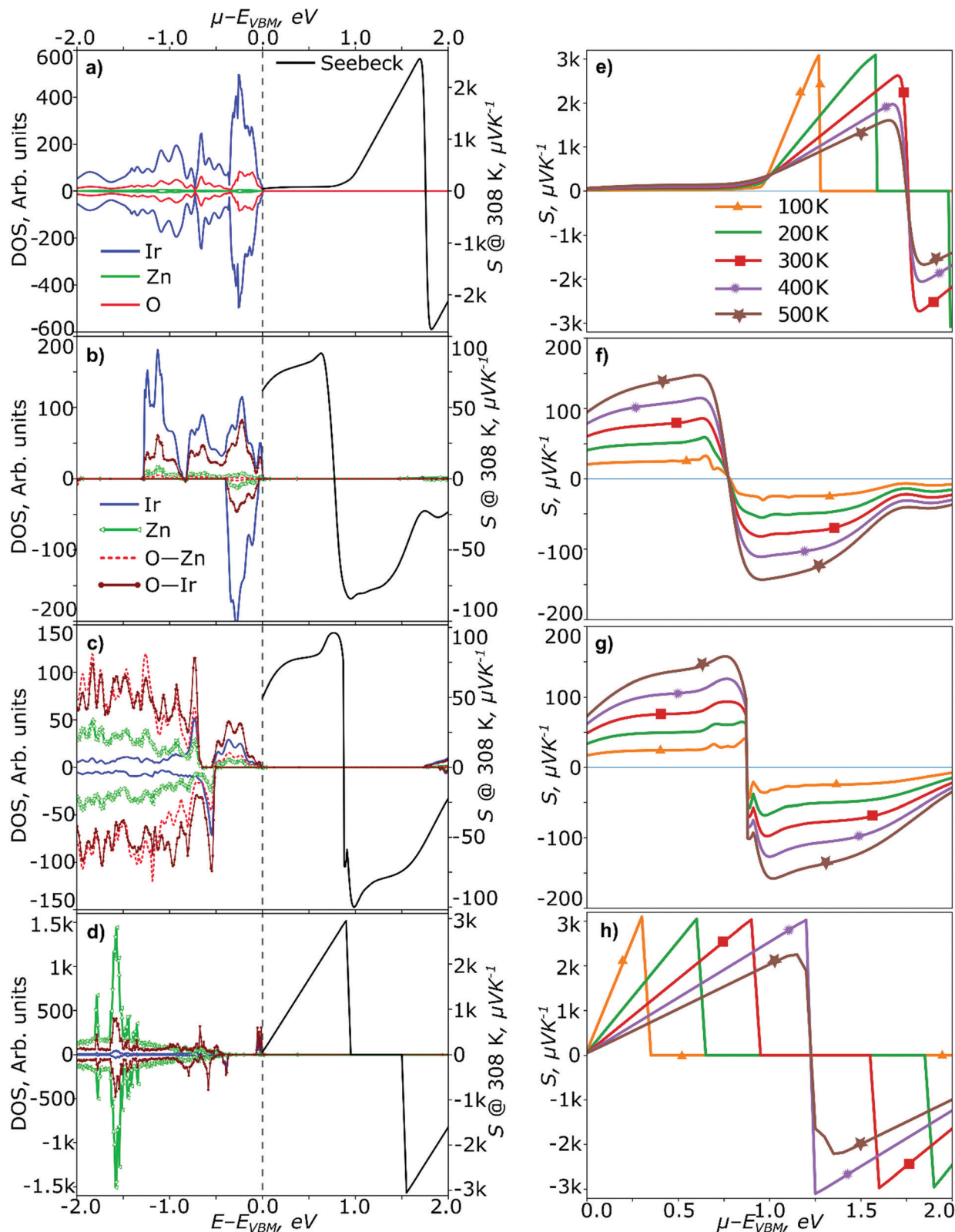


Fig. 7 Left panel: The partial DOS as a function of $E - E_{VBM}$ (left-bottom axis) and Seebeck coefficient (S , black curve) at $T = 308$ K as a function of Fermi level $\mu_F = \mu - E_{VBM}$ (top-right axis). The valence band maximum (E_{VBM}) is taken as zero (grey dashed line). DOS lines are smoothed with a cubic spline. No scaling is applied. Right panel: $S(\mu_F)$ for a range of temperatures. ZnIr_2O_4 : (a) and (e), Ir^{2+}O_4 : (b) and (f), Ir^{4+}O_6 in L4: (c) and (g), Ir^{4+}O_6 in L48: (d) and (h). The O-Ir line describes the oxygens surrounding Ir, whereas the O-Zn line is for all the other oxygens in the supercell.



surrounding Ir (Ir–O band). It is the band of the width of ~ 0.4 eV (small supercell, L4). The states of the same oxygens are extended to deeper energies and hybridized with the states of other oxygens in the lattice (the total width of this band is around 5 eV). The Zn states contribute at even deeper energies. In the large supercell (L48, Fig. 7d), the Ir–O band is separated from the extended O-band which should have an impact on the calculated thermoelectric properties. The band gap in Ir-doped ZnO is between the occupied and unoccupied Ir–O bands and changes from 1.75 to 2.50 eV for the small (L4, $c = 12.50\%$) and large (L48, $c = 1.04\%$) supercell.

Even though the overall characteristics in the calculated complexes are similar, there are still some differences to mention (Fig. S2, ESI[†] and Fig. 7b). The hybridization effect as discussed above is stronger in Ir³⁺O₄ than in Ir⁴⁺O₆. Essentially, the top of the valence band in Ir³⁺O₄ is formed of Ir states and all oxygens in the lattice. In the case of the Ir⁴⁺O₅ complex, the picture is similar with Ir⁴⁺O₆, but the Ir–O band is wider (almost 1 eV).

Analysis of thermoelectric properties

In the present analysis, we discuss the calculated thermoelectric properties, *i.e.* the Seebeck coefficient (S) and electrical conductivity (σ), for the IrO_x complexes in ZnO and reference systems: perfect ZnO, ZnIr₂O₄ and IrO₂. Thermoelectric properties are extremely sensitive to the electronic structure. Perfect ZnO is not expected to demonstrate good potential for the p-type conduction. We suggest that this property of ZnO is reflected in the steep increase of the calculated S to unrealistically high values (see Fig. S2a, ESI[†]) in the proximity of VBM.

In the calculations the exact Fermi level μ_F is unknown but a comparison with the available experimental data could help with its identification. Therefore, S and σ dependence on μ_F referenced at the VBM, *i.e.* $S(\mu_F)$ and $\sigma(\mu_F)$, lies at the heart of our analysis. Typically, such dependencies have two parts for positive and negative values of S standing for holes and electrons, respectively. We, therefore, focus our analysis on

the positive S -values only to estimate the potential of Ir-doped ZnO for the p-type conduction.

In Table 4 the calculated σ - and S -values at fixed μ_F are compared with the corresponding data found in the experimental literature and our previous experimental results.¹⁰ Notice that the experimental results differ by the sample preparation and treatment, leading to some scatter in data. Interestingly, it is almost the same value of $\mu_F = \mu - E_{\text{VBM}} \approx 0.7$ eV for all systems for both S and σ in Table 4 to find better correspondence with the experimental values and is, therefore, a good compromise for such a comparison.

The calculated σ -value for ZnIr₂O₄ and IrO₂ agree very well with the experimental data. The cation vacancies and anti-sites are detrimental defects in spinels^{13,67} explaining, at least in part, the p-type conductivity. Thus, it should be reflected in the S -values as well. Indeed, we emphasize significant differences in the behaviour of $S(\mu_F)$ for bulk ZnIr₂O₄ in a comparison with perfect ZnO. It has a well distinguished plateau in the range of μ_F between 0 and 0.8 eV (Fig. 7a) followed by a steep increase to very high values. A positive Seebeck coefficient of $92.3 \mu\text{V K}^{-1}$ at $\mu_F = 0.7$ eV is in agreement with the experimental values (Table 4).

The Ir-doped ZnO is characterized by a high sensitivity of thermoelectric properties to the electronic structure as well. All IrO_x complexes as discussed in the present study show different behaviour of $S(\mu_F)$. However, we again emphasize the presence of a plateau and steep increase to very high values for some of the complexes. The positive Seebeck coefficient is in the range 60–80 and 55–90 $\mu\text{V K}^{-1}$ for the complex without the interstitial oxygens, (Ir²⁺O₄), and in the Ir⁴⁺O₆ complex in the small supercell ($c = 12.5\%$, L4), respectively, depending on μ_F (in the range of μ_F between 0 and 0.8 eV) at 308 K. Neither the Ir²⁺O₄ nor Ir⁴⁺O₆ complex in the small supercell (L4) are characterized by the steep increase of $S(\mu_F)$ as were found in perfect ZnO and ZnIr₂O₄. Here $S(\mu_F)$ increases smoothly approaching the maximum value at $\mu_F \sim 0.70$ – 0.75 eV (Fig. 7b and c). In contrast, the Ir⁴⁺O₅ and Ir³⁺O₄ complexes

Table 4 Calculated thermoelectric properties. S is the Seebeck coefficient, σ is the electrical conductivity and c is the Ir concentration. Only the maximal component of the S tensors is given for the Fermi level $\mu_F = \mu - E_{\text{VBM}} = 0.7$ eV. All the calculated and measured properties are given at 308 K, if not otherwise stated

Compound	S , $\mu\text{V K}^{-1}$	S exp, $\mu\text{V K}^{-1}$	σ , $\Omega^{-1} \text{m}^{-1}$	σ exp, $\Omega^{-1} \text{m}^{-1}$
ZnO	2510	Non-conducting	6.05×10^{-8}	Non-conducting
ZnIr ₂ O ₄	92.3	53.9 ^a 68	1.72×10^2	2.09×10^2 , 3.39×10^{2a} 68
IrO ₂	63.9	—	1.32×10^6	1.15 – 2.90×10^6 69,70 0.68 – 1.67×10^6 ^b 71 2.94×10^6 ^c 71
Ir ₂ O ₃	105	—	8.98×10^1	—
Ir ²⁺ O ₄	80.1	6.8^d 10	2.57×10^2	47.6^d 10
Ir ³⁺ O ₄	88.7	—	3.20×10^1	—
Ir ⁴⁺ O ₅	89.4	—	4.13×10^1	—
Ir ⁴⁺ O ₆ ($c = 12.5\%$, L4)	83.8	—	1.62×10^2	—
Ir ⁴⁺ O ₆ ($c = 1.04\%$, L48)	2335	—	3.49×10^{-8}	—

^a Measured at room temperature; two values for σ for polycrystalline and epitaxial thin films whereas the Seebeck coefficient was measured for polycrystalline films only; the thin films prepared by PLD between 773 and 973 K. ^b The values are taken at room temperature for the 100 nm thin films prepared by PLD and oxidized at 0.05–0.2 mBar and 500 °C. ^c The bulk value measured at room temperature. ^d The Ir concentration $c = 16.4\%$.



(Fig. S2, ESI†) show very similar behavior of $S(\mu_F)$ with ZnIr_2O_4 and demonstrate much smaller changes for the S -values in the range of μ_F between 0 and 0.8 eV. In Fig. S2b and c (ESI†) it is demonstrated that the plateau in the range of μ_F between 0 and 0.8 eV is present and leads to the values of S of the order of $\sim 89 \mu\text{V K}^{-1}$ (see also Table 4). The presence of a plateau and formation of O_2^{2-} are, in our opinion, interconnected.

We do not expect perfect agreement for the absolute S -values between the experiment and simplified model in the calculation but rather present a qualitative picture explaining the p-type conduction in Ir-doped ZnO. Also, we notice a significant decrease of σ for the Ir concentration $c = 1.04\%$ (Ir^{4+}O_6 , L48). In this case there is again a steep increase of the calculated S to very high values (see Fig. 7d) in the proximity of VBM similar to perfect ZnO. In the complexes with the plateau, the steep increase is shifted to higher μ_F . At the values of $\mu_F = 0.8\text{--}1.9$ eV for Ir^{3+}O_4 and $0.8\text{--}1.6$ for Ir^{4+}O_5 the steep increase of S is observed and transformation into the n-type conductor follows. Furthermore, $S(\mu_F)$ is differently influenced by temperature T in the two ranges of μ_F , $0.0 < \mu_F \leq 0.8$ eV and $0.8 < \mu_F \leq 1.9(1.6)$ eV, in Fig. 7(f–h) and Fig. S2(d and e) (ESI†). At $\mu_F \leq 0.8$ eV, $S(\mu_F)$ increases with T , and an opposite behaviour is found in the range $0.8 < \mu_F \leq 1.9(1.6)$ eV for the complexes with the steep increase. Qualitatively speaking, this picture is very close to what was observed for ZnIr_2O_4 as well (Fig. 7e).

Conclusions

We have successfully combined hybrid DFT calculations and Ir L_3 -edge XAS experiments to gain insight into the local atomic structure around iridium ions in Ir-doped ZnO. The $\text{ZnO}:c\text{Ir}$ ($c = 7\%, 16\%, 29\%, 54\%$ and 67%) and IrO_x thin films of thickness 200–300 nm were deposited by reactive DC magnetron co-sputtering on polyimide tape substrates. The role of interstitial oxygens was emphasized in such experiments. Thus, the analysis of EXAFS spectra using the reverse Monte Carlo simulations revealed that iridium ions are predominantly octahedrally coordinated by oxygens. Consequently, several IrO_x ($x = 4\text{--}6$) polyhedra (complexes) inside the wurtzite ZnO lattice were selected for the calculations of the atomic and electronic structure, vibrational and thermoelectric properties from the first principles.

The hybrid PBE0 exchange–correlation functional and Gaussian basis-set described very well the basic properties of ZnO, ZnIr_2O_4 , and IrO_2 crystals, which justified further computational study of Ir-doped ZnO. The complexes (Ir^nO_x) were distinguished by the oxidation state of Ir (n) and formation of peroxide defects, and as a consequence, by the different number of oxygens (x) surrounding Ir ions. Their corresponding formulas were chosen as Ir^{2+}O_4 – the system without interstitial oxygens O_i 's, Ir^{3+}O_4 – the first system with the interstitials and formation of peroxide defects O_2^{2-} , Ir^{4+}O_5 – the second system with the formation of peroxide defect, and lastly, Ir^{4+}O_6 the system with Ir ions which are octahedrally coordinated by

oxygens. It is worth mentioning that the selected complexes containing two interstitial O_i ions were found by a careful treatment of numerous spatial configurations with different total energies. However, we were able to choose the three most important ones and focus our study on the analysis of the relevant Seebeck coefficient, electrical conductivity and density of states for them. Moreover, the Ir^{4+}O_6 complex was calculated with two Ir concentrations, namely 12.50 and 1.04%. We compared the calculated thermoelectric properties for the chosen complexes with those for the reference systems, *i.e.* perfect ZnO, ZnIr_2O_4 , and IrO_2 . Each calculated IrO_x complex demonstrated some differences in the calculated DOS. However, the main DOS feature of calculated complexes for the Ir concentration 12.5% is due to (1) the mixed Ir–O band contributing to the VBM, (2) the states of oxygens surrounding Ir and their extension and hybridization with the other oxygens states in the lattice, and (3) as a consequence, the predicted positive Seebeck coefficient and electrical conductivity for the Fermi level μ_F (referenced at the VBM) lying in the range $0 \leq \mu_F \leq 0.8$ eV. In this μ_F -range the calculated Seebeck coefficients are close for the four calculated complexes including the one without O_i 's. In contrast, the calculation of smaller Ir concentration (1.04%) for the Ir^{4+}O_6 complex revealed the Seebeck coefficient behaviour similar with the hypothetical perfect ZnO which is reflected in its steep increase in the proximity of VBM. It can be explained by a separate Ir–O band characterized by much weaker hybridization effect with the host oxygens and smaller width in a comparison with the larger concentration 12.5%. Such differences between the Ir concentrations should explain the sign change in the Seebeck coefficient behaviour observed experimentally in ref. 10. Lastly, the calculated local vibrational frequencies of O_2^{2-} peroxides entering two complexes, Ir^{3+}O_4 and Ir^{4+}O_5 , are close to those in the Raman measurements in ref. 10. The complexes with the formation of peroxide defects, *i.e.* Ir^{3+}O_4 (Ir^{4+}O_5), also have the steep increase of Seebeck coefficient in the range $0.8 < \mu_F \leq 1.9(1.6)$ eV similar to ZnIr_2O_4 .

Author contributions

A. C.: investigation, formal analysis, writing – original draft, visualization. D. G.: methodology, writing – review & editing. N. V. S.: project administration, supervision. E. A. K.: project administration, supervision. A. Z.: investigation, M. Z.: investigation. A. K.: investigation, formal analysis, writing – review & editing, visualization. A. A.: investigation. J. P.: funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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