Revisiting isoreticular MOFs of alkaline earth metals: a comprehensive study on phase stability, electronic structure, chemical bonding, and optical properties of A–IRMOF-1 (A = Be, Mg, Ca, Sr, Ba)

Li-Ming Yang,*a Ponniah Vajeeston, b Ponniah Ravindran, b Helmer Fjellvåg b and Mats Tilset∗a

Received 22nd December 2010, Accepted 23rd March 2011
DOI: 10.1039/c0cp02944k

Formation energies, chemical bonding, electronic structure, and optical properties of metal–organic frameworks of alkaline earth metals, A–IRMOF-1 (where A = Be, Mg, Ca, Sr, or Ba), have been systemically investigated with DFT methods. The unit cell volumes and atomic positions were fully optimized with the Perdew–Burke–Ernzerhof functional. By fitting the E–V data into the Murnaghan, Birch and Universal equation of states (UEOS), the bulk modulus and its pressure derivative were estimated and provided almost identical results. The data indicate that the A–IRMOF-1 series are soft materials. The estimated bandgap values are all ca. 3.5 eV, indicating a nonmetallic behavior which is essentially metal independent within this A–IRMOF-1 series. The calculated formation energies for the A–IRMOF-1 series are −61.69 (Be), −62.53 (Mg), −66.56 (Ca), −65.34 (Sr), and −64.12 (Ba) kJ mol⁻¹ and are substantially more negative than that of Zn-based IRMOF-1 (MOF-5) at −46.02 kJ mol⁻¹. From the thermodynamic point of view, the A–IRMOF-1 compounds are therefore even more stable than the well-known MOF-5. The linear optical properties of the A–IRMOF-1 series were systematically investigated. The detailed analysis of chemical bonding in the A–IRMOF-1 series reveals the nature of the A–O, O–C, H–C, and C–C bonds, i.e., A–O is a mainly ionic interaction with a metal dependent degree of covalency. The O–C, H–C, and C–C bonding interactions are as anticipated mainly covalent in character. Furthermore it is found that the geometry and electronic structures of the presently considered MOFs are not very sensitive to the k-point mesh involved in the calculations. Importantly, this suggests that sampling with Γ-point only will give reliable structural properties for MOFs. Thus, computational simulations should be readily extended to even more complicated MOF systems.

I. Introduction

Metal–organic frameworks (MOFs) are composed of metal ions or metal clusters as nodes and multitopic organic ligands as linkers, and have received considerable attention over the last decade because of their potential applications in gas adsorption and storage, separation, catalysis, sensing, molecular recognition, and much more, as has been recently reviewed.1 Although the structure and internal environment of the pores in MOFs can in principle be controlled through judicious selection of nodes and organic linkers, the direct synthesis of such materials with desired functionalities in the pores or channels is often difficult to achieve due to their thermal/chemical sensitivity or high reactivity. New MOFs continue to appear at a very high pace due to differences in procedures for their preparation and handling in different research groups.2 Recently, Yaghi and coworkers proposed a reticular synthesis3,4 approach and designed a series of IRMOFs (i.e., IRMOF-1 to IRMOF-16).5 These IRMOFs have the same underlying topology but a different chemical functionality of the pores via different ligands. Introduction of functionality at the pores may allow for enhanced hydrogen and methane storage capabilities.5, 6

a Center of Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, Box 1033 Blindern, N-0315, Oslo, Norway. E-mail: mats.tilset@kjemi.uio.no, l.m.yang@kjemi.uio.no; Fax: +47 22855441
b Center for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Box 1033 Blindern, N-0315, Oslo, Norway

† Electronic supplementary information (ESI) available: Optimized bond lengths (Å) and bond angles (°), the plot of calculated Bader charges (BC), bond overlap populations (BOP) and Mulliken effective charges (MEC) for the A–IRMOF-1 series (A = Be, Mg, Ca, Sr, Ba). Partial density of states (PDOS), band structures and optical properties of A–IRMOF-1 (A = Mg, Ca, Sr and Ba). See DOI: 10.1039/c0cp02944k
On the other hand, computational chemistry and physics have made dramatic advances in the past two decades, enabling the prediction of novel molecules and exotic extended structures that often contradict the chemical and physical intuitions. Many theoretical chemists and physicists have participated in this endeavor by proposing myriads of unusual molecules and bulk solid structures. The computational simulations are a powerful tool to predict new materials as well as their properties and can provide insight into the prerequisite experimental aspects. Most publications relating to MOFs are experimental in nature owing to the fact that the number of atoms involved in simulations is much greater than that in many other materials. Thousands of different MOFs have been synthesized so far. However, the enormous number of different possible MOFs means that purely experimental means for screening or designing optimal MOFs for targeted applications is inefficient. Atomic-level simulations provide a means to complement experimental methods for identifying potential MOFs. In this contribution, we aim to show that electronic structure calculations and chemical bonding analysis can help one to acquire insight into the properties of the MOF series A–IRMOF-1 (A = Be, Mg, Ca, Sr, Ba).

In this work, we would like to assert whether different alkaline-earth metals can be used to build up such materials and if so, to investigate how the chemical bonding and electronic structures of the materials depend on the identity of the cornerstone metal. As an initial step, consider the archetypical IRMOF-1 (MOF-5) as an example. As a few A–IRMOF-1 species (A = Be, Mg, and Ca) have been calculated within the local density approximation (LDA) with ultrasoft Vanderbilt-type pseudopotentials. However, the generalized gradient approximation (GGA) which includes the effects of local gradients in the charge density for each point in the crystal generally gives better equilibrium structural parameters than the LDA. This motivated us to perform calculations using the GGA functional to check the reliability of the reported LDA results.

Moreover, to the best of our knowledge, some key properties such as the formation energies, optical properties, and chemical bonding in A–IRMOF-1 have not yet been studied systematically. The formation enthalpy is a property well suited to help establish whether theoretically predicted phases are likely to be stable and such data may also serve as guides for possible synthesis routes. The optical properties will provide valuable information about the occupied and unoccupied parts of the electronic structure and also the character of the bands. Furthermore, these data will provide relevant information for their potential uses in hybrid solar cell applications, whether as an active material or in the buffer layer between the electrodes and inorganic active materials.

Fig. 1 The topology of the hypothetical A–IRMOF-1 (A = Be, Mg, Ca, Sr, Ba) series in the cubic \( Pm\bar{3}m \) symmetry (no. 225) is shown in (a), the corresponding linker and node are shown in (b) and (c), respectively. We distinguish the atoms with labels \( A = \text{Be, Mg, Ca, Sr, and Ba} \), O1, O2, C1, C2, C3, and H for the interpretation and understanding of partial density of states (PDOS) in the electronic structure section.

The bonding interaction between constituents is important to understand chemical and physical properties of a system. The establishment of the nature of chemical bonding between components in A–IRMOF-1 is quite crucial since such an insight can be used to evaluate structural, thermodynamic, and other physical properties of the materials. Next, this may assist the design of modified structures in such a way to enhance their value in applications such as gas absorption, catalysis, sensing, and molecular recognition.

In this work we have performed a comprehensive theoretical study of the solid-state structures, electronic structures, formation energies, and chemical bonding in A–IRMOF-1 compounds using the GGA-PBE functional calculation based on DFT as implemented in the VASP code. For the optical properties, Mulliken charge analysis, and bond overlap population calculations, we have employed the CASTEP code. As a few A–IRMOF-1 species (A = Be, Mg, and Ca) have already been investigated, our goals have included: (1) to extend this study into higher analogues, \( i.e. \), Sr and Ba, so as to get the general trends and rules for the properties of the complete range of alkaline-earth metals; (2) to test the results obtained from LDA calculations using GGA; (3) to provide a more comprehensive understanding of chemical bonding within this series; and (4) to predict the optical properties to prepare the ground for designing potential MOFs as photocatalysts and active components in hybrid solar cells and electroluminescence cells.
II. Computational details

The Vienna *ab initio* simulation package (VASP)\(^{13,14}\) has been used for the structural optimization to study the structural stability and to establish equilibrium structural parameters. The GGA\(^{10–12}\) includes the effects of local gradients in the charge density for each point in the lattice, which generally gives better equilibrium structural parameters than the LDA. Hence, we have used the Perdew, Burke, and Ernzerhof (PBE)\(^{12}\) GGA functional for all our calculations. The projector-augmented-wave (PAW)\(^{14,16}\) pseudo-potential was used to describe the ion-electron interactions. The basis set in the calculation involves the valence configurations of 2s\(^2\), 3s\(^2\), 3p\(^6\)4s\(^2\), 4s\(^2\)4p\(^6\)5s\(^2\), and 5s\(^2\)5p\(^6\)6s\(^2\) for Be, Mg, Ca, Sr, and Ba, respectively. The valence electron configurations considered in the calculation for O, C, and H are 2s\(^2\)2p\(^2\), 2s\(^2\)2p\(^2\), and 1s\(^1\), respectively. It may be noted that, for the alkaline-earth metals with high atomic numbers, it is important to consider the semicore states in order to correctly predict the structural properties. Hence, we have included semicore p-electrons into the calculations for systems containing Ca, Sr, and Ba. A criterion of 0.01 meV atom\(^{-1}\) was placed on the self-consistent convergence of the total energy. All the calculations were made with the plane-wave cutoff of 500 eV, which guarantees that absolute energies are converged to within a few meV per formula unit. The Brillouin-zone integration was performed with a Gaussian broadening of 0.2 eV during all relaxations. The conjugated-gradient algorithm based on Hellmann–Feynman forces was used to relax the ions into their instantaneous equilibrium positions. The forces and the stress tensor were used to determine the search directions for localizing the ground state (*i.e.*, the total energy is not taken into account). This algorithm is very fast and efficient when the initial structures are far away from the ground state. Forces on the ions were calculated using the Hellmann–Feynman theorem as the partial derivatives of the free electronic energy with respect to the atomic positions and adjusted using the Harris-Foulkes correction to the forces. The atoms were relaxed toward equilibrium until the Hellmann–Feynman forces were less than 10\(^{-3}\) eV Å\(^{-1}\).

In order to understand the effect of k-points on the optimized crystal structure and electronic structure, we have made comparisons of optimized structural parameters and densities of state (DOS) calculated with different k-point sets. First, geometry optimization was performed with the \(\Gamma\)-point alone. On the basis of optimized geometry with the \(\Gamma\)-point, the geometry was reoptimized with the k-point grid of \(2 \times 2 \times 2\) using the Monkhorst–Pack scheme. We found that the results are nearly identical for these two k-point meshes. In order to have accurate band structures and density of states, we have performed the DOS calculations on the fully optimized structure with the k-point grid of \(3 \times 3 \times 3\) using the Monkhorst–Pack scheme as well as the \(\Gamma\)-point only for comparison.

For the exploration of possible approaches to synthesis of these compounds we have also computed the total energy for C (R3m), O\(_2\) (P4/mmm), H\(_2\) (P4/mmm), Zn (P6\(_3\)/mmc), Be (P6\(_3\)/mmc), Mg (P6\(_3\)/mmc), Ca (Fm\(_{3m}\)), Sr (Fm\(_{3m}\)), and Ba (Im\(_{3m}\)) in their ground state structures with full geometry optimization. The reaction enthalpies were calculated from the total energy of the reactants and products involved in the reactions concerned. The validity of such an approach has been tested and found to be satisfactory for known hydride phases.\(^{17,18}\) Even though temperature effects were not included in this approach, one can reliably reproduce or predict formation enthalpies, *viz.* temperature effects roughly cancel owing to similarities in the phonon spectra among reactants and products. To gauge the bond strength and character of bonding we have analyzed bond overlap population (BOP) values with on the fly pseudopotentials estimated on the basis of the Mulliken population analysis as implemented in the CASTEP code.\(^{15}\)

In order to understand the chemical bonding and interactions between constituents in the A–IRMOF-1 series, we have performed charge density, charge transfer, and electron localization function (ELF)\(^{19–22}\) analyses. Moreover, detailed Bader charge analyses of the A–IRMOF-1 series were undertaken. The linear optical properties, including adsorption coefficient, reflectivity, refractive index, optical conductivity, dielectric function, and energy loss function, have been calculated with ultrasoft pseudopotentials for all these compounds using the CASTEP code. In parallel with the optical properties we have also calculated the band structure for all the A–IRMOF-1 compounds using the CASTEP code, and from these results the band gap, optical transitions and the behavior of carriers can be assessed.

III. Results and discussion

A Structural details

The 3D structures of the members of the A–IRMOF-1 series have been taken to be similar to that of crystallographically characterized IRMOF-1 (MOF-5). MOF-5 is the first member of a series of isoreticular metal–organic frameworks (IRMOF) based on the reticular synthesis chemistry introduced by Yaghi and coworkers.\(^{3,4}\) The MOF-5 solid-state structure (Fig. 1a) consists of inorganic oxide-centered ZnO tetrahedra as nodes (see Fig. 1c) linked by organic 1,4-benzenedicarboxylate (BDC) units (see Fig. 1b) as linkers. It should be pointed out that, depending upon the synthesis process and experimental conditions, residual ZnO species may interpenetrate the pores and lattice such that the crystal symmetry may change from cubic to trigonal, a factor which may affect the physical and chemical properties of the material.\(^{23}\)

In this work, we have used the structural details of the well-characterized crystalline phase of IRMOF-1 with cubic *Fm\(_{3m}\)* symmetry (no. 225) as an input for all our calculations. The conventional cell of the hypothetical A–IRMOF-1 series includes eight formula units *A*\(_6\)O(BDC)\(_3\)* (where *A* = Be, Mg, Ca, Sr, Ba). Its primitive cell includes two nodes and six linker molecules, corresponding to two *A*\(_6\)O(BDC)\(_3\) formula units and the topology of the corresponding 3D structure of A–IRMOF-1 is illustrated in Fig. 1. The different atomic sites in A–IRMOF-1 include one type of A, two types of O, three types of C, and one type of H that occupy 32f, 8c, 96k, 48g, 48g, 96k, and 96k Wyckoff positions, respectively.
B Results from structural optimization of A–IRMOF-1

In order to acquire the ground-state predicted structures from the theoretical calculations, the hypothetical structures were built by replacing the Zn atoms in MOF-5 (IRMOF-1) with alkaline earth metal atoms (A = Be, Mg, Ca, Sr, Ba) such that the experimental (crystallographic) structural parameters of IRMOF-1 were used as the initial guess for the entire A–IRMOF-1 series. The equilibrium theoretical structures were obtained from full geometry optimization, i.e., with fully relaxed atomic positions and cell parameters.

The atomic positions were first relaxed globally using the force-minimization technique by keeping the lattice constant (a) and cell volume (V) fixed to the experimental equilibrium values for MOF-5 used as the initial guess. The theoretical equilibrium volume was then determined with optimized atomic positions by varying the cell volume within ±10% of the experimental equilibrium volume of MOF-5. The calculated total energy as a function of volume (E–V) was fitted to the so-called equation of state (EOS) to calculate the bulk modulus (B0) and its pressure derivative (B0′). In order to cross check the calculated B0 and B0′ values, the E–V data were fitted into three different EOS, i.e., Murnaghan,24 Birch–Murnaghan,25 and Universal equation of states (UEOS).26 The bulk moduli and their pressure derivatives (in parentheses) obtained from the E–V curve using the UEOS are 19.55 GPa (3.32) for A = Be, 14.94 GPa (4.39) for Mg, 12.16 GPa (3.46) for Ca, 10.73 GPa (4.11) for Sr, and 9.37 GPa (4.07) for Ba in the A–IRMOF-1 series. The corresponding results derived from the two other EOSs can be found in Table 1. From these results one can conclude that the B0 and B0′ values estimated from three different EOS derived from the E–V data are nearly identical. Moreover, the bulk modulus decreases monotonically when one moves from Be to Ba, and its pressure derivatives are almost constant within this series. It may be noted that the presently calculated B0 values are found to be comparable with the values of 21.103, 15.657, and 12.262 GPa for the A–IRMOF-1 species (A = Be, Mg, Ca, respectively) that were investigated previously by VASP calculation within LDA by fitting of the total energy with Birch–Murnaghan EOS.9 There are as yet no experimentally measured bulk modulus values available for any of these compounds with which to compare our results.

The calculated equilibrium lattice parameters, bond lengths, and bond angles along with those available from the earlier computational study for A–IRMOF-1 (A = Be, Mg, Ca) are listed in Table S1 (in ESIF). The presently calculated values of equilibrium structural parameters are comparable to those reported earlier.9 From Table 1 and Table S1 (ESIF), it can be concluded that the optimized structural parameters from different k-point set (Γ and 2 × 2 × 2 k-point) calculations for the A–IRMOF-1 series are nearly identical. The insensitivity of the optimized structural parameters to different k-point meshes is attributed to the insulating behavior with dispersionless band distribution. Moreover, the large size of the primitive cell involved in the calculations makes the volume of the Brillouin-zone small, and thus the Γ-point only calculation itself gives well converged structural parameters for the A–IRMOF-1 series. Usually, MOFs are relatively big systems with a large number of atoms involved in the calculations, which inevitably may lead to difficulties in accurate computational modeling compared with what is the case for smaller, molecular systems. Our conclusion concerning the insensitivity of the structural parameters to the k-point mesh is very encouraging for computational chemists who are interested in theoretical modeling of MOFs. The present study suggests that one can use the Γ-point only mesh alone for such calculations, a finding which will dramatically reduce the already severe requirements for computational resources.

C Energy of formation considerations

Data on formation enthalpies constitute an excellent means to establish whether theoretically predicted phases are likely to be stable, and such data may serve as a guide to evaluate possible synthesis routes. For the exploration of the thermodynamic feasibility of accessing these compounds from the elements (eqn (1)) we have also computed the total energies for C (R3m), O2 (P4/mmm), H2 (I4/mmm), Zn (P63/mmc), Be (P63/mmc), Mg (P63/mmc), Ca (Fm3m), Sr (Fm3m), and Ba (Im3m) in their ground state structures with full geometry optimization. The reaction enthalpies for MOF formation were calculated from the difference in the total energy between the products and reactants involved in the reactions concerned and are summarized in Table 2. The results establish unambiguously that eqn (1) expresses exothermic reactions for IRMOF-1 as well as for the hypothetical A–IRMOF-1 series.

\[
8A + 13O_2 + 48C + 12H_2 \rightarrow A_8O_{26}C_{48}H_{24} \quad (A = Zn, Be, Mg, Ca, Sr, Ba)
\]

(1)

<table>
<thead>
<tr>
<th>A–IRMOF-1</th>
<th>(d_0^a) Å</th>
<th>(B_0^h) GPa</th>
<th>(B_0'^h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>24.3596</td>
<td>19.55</td>
<td>3.33</td>
</tr>
<tr>
<td>Mg</td>
<td>26.1521</td>
<td>14.94</td>
<td>4.39</td>
</tr>
<tr>
<td>Ca</td>
<td>27.7486</td>
<td>12.16</td>
<td>3.46</td>
</tr>
<tr>
<td>Sr</td>
<td>28.6361</td>
<td>10.73</td>
<td>4.11</td>
</tr>
<tr>
<td>Ba</td>
<td>29.5670</td>
<td>9.37</td>
<td>4.09</td>
</tr>
</tbody>
</table>

The optimized equilibrium lattice constant \((a)\) in italic and bold fonts are from Γ-point and 2 × 2 × 2 k-point calculations, respectively. Data in (braces) are from ref. 9. Data without brackets from Universal EOS; data in parentheses from Murnaghan EOS; data in [braces] from Birch–Murnaghan 3rd-order EOS; data in (braces) from ref. 9.

<table>
<thead>
<tr>
<th>A</th>
<th>Zn</th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH/kJ mol(^{-1})</td>
<td>-46.02</td>
<td>-61.69</td>
<td>-62.53</td>
<td>-66.56</td>
<td>-65.34</td>
<td>-64.12</td>
</tr>
</tbody>
</table>

Table 1 Optimized equilibrium lattice constant \((a)\) Å, bulk modulus \((B_0)\) GPa, and its pressure derivative \((B_0')\) for A–IRMOF-1 (A = Be, Mg, Ca, Sr, Ba)

Table 2 Calculated enthalpies of formation (ΔH) kJ mol\(^{-1}\) for the prototypical IRMOF-1 (A = Zn) and A–IRMOF-1 (A = Be, Mg, Ca, Sr, Ba) compounds
The formation energy for the prototypical MOF-5 is \(-46.02\, \text{kJ mol}^{-1}\), indicating that MOF-5 is a thermodynamically stable phase at ambient conditions. This has already been established by a series of experimental and theoretical studies. Our estimated large negative values for the enthalpy of formation for the A–IRMOF-1 series also suggest that it might be possible to synthesize these compounds as stable phases. The magnitudes of the calculated formation enthalpies given in Table 2 suggest that (1) the A–IRMOF-1 series is more stable than IRMOF-1 (MOF-5), and (2) the stabilities of these A–IRMOF-1 compounds are very similar since they have comparable formation enthalpies.

Interestingly, and consistent with the above viewpoint, the first microporous beryllium coordination polymer, i.e., Be–BDC, has recently been reported. Powder X-ray diffraction measurements on Be–BDC indicate the formation of a large unit cell—a unit cell that is larger in at least one cell parameter compared to MOF-5, or possessing lower symmetry. Although structural ambiguities have yet to be resolved (due to the limitations in phase purity), it is now clear that such highly porous materials may in principle, from a thermodynamic point of view, be obtained even with light metals such as Be. Note however that reaction kinetics during syntheses are not taken into account, and that temperature effects (e.g., entropy contributions) have not been included in the present calculations. It will be interesting to see if future attempts at synthesizing these materials will be successful, as the present study suggests that it should be possible to access all the compounds in the A–IRMOF-1 series.

Most MOFs are synthesized through solvothermal methods. Reagents are typically sealed in a PTFE lined autoclave in the chosen solvent and heated to between 100 and 250 °C where the above-atmospheric pressure maintains the condensed-phase reaction environment. This allows to surpass the activation barrier such that the complex framework structures can be effectively assembled without evaporation of the solvent. This process often results in single crystals sufficiently large to be suitable for single-crystal X-ray diffraction analysis (or at least powder X diffraction), which will provide complete experimental structural information. The present observation of negative formation energies for all these phases suggests that experimentalists should try new synthetic methods.

**D Variation of calculated DOS with a number of k-points in A–IRMOF-1**

In order to perform efficient computations, it is important to know the effect of the number of k-points used in the calculation of the total and partial DOS of the MOFs, since the number of atoms involved in the calculations is usually very large. MOFs represent porous materials that usually have somewhat limited thermal as well as chemical stabilities, and considerable freedom exists to build crystals of diverse topologies and connectivities within the large unit cells. In these

---

**Fig. 2** Calculated partial density of states (PDOS) for Be–IRMOF-1 obtained from (a) \( \Gamma \) point \((1 \times 1 \times 1)\) only \(\mathbf{k}\)-mesh and (b) \(3 \times 3 \times 3\) \(\mathbf{k}\)-mesh using the Monkhorst–Pack scheme.
materials, interactions between atoms of the spatially separated, adjacent nodes or linkers will be rather weak. This leads to rather dispersionless (i.e., very flat) band structures of the MOFs, and hence the bands seldom cross each other in the band structure plot. As a result, there are many isolated peaks in the DOS plots of MOF materials. In contrast, the interactions between adjacent atoms are usually strong for more closely compacted materials, resulting in well dispersed band structure plots. For such materials, one often needs higher density \( k \)-points to estimate the DOS reliably.

From the experience in calculating DOS for the A–IRMOF-1 series of MOFs (see Fig. 2) we have found that the DOS of MOFs are not very sensitive to the \( k \)-points compared to the situation for other materials, i.e., the DOS with \( \Gamma \)-point only are almost the same as that with higher density \( k \)-points (e.g., \( 3 \times 3 \times 3 \) using the Monkhorst–Pack scheme), since the interactions between atoms of adjacent nodes are weak. Only directly connected atoms have strong chemical bonding interactions, like in molecules. As the calculated DOS from two different sets of \( k \)-points are found to be almost identical in Fig. 2, we suggest that the \( \Gamma \)-point only DOS are sufficient to describe the properties qualitatively in MOF materials such as the A–IRMOF-1 series studied here. It should be noted that this will save substantial computing resources (CPU hours, memory, etc.) without significant losses in accuracy. As the features such as dispersionless electronic structure are essentially common to all MOFs, we expect that these considerations may be general for all MOF materials.

In the following sections we will make detailed comparisons of A–IRMOF-1 by \( \Gamma \)-point only calculations and by \( 3 \times 3 \times 3 \) \( k \)-points calculations using the Monkhorst–Pack scheme, and show how changes in the number of \( k \)-points in the calculations affect the results. In order to simplify the discussion, we have displayed below only the DOS of the representative case Be–IRMOF-1. The remaining members of the series can be found in the ESI.<ref>

From the comparison of the DOS for the A–IRMOF-1 series obtained from two different sets of \( k \)-points we conclude that the \( \Gamma \)-point only calculations can display the DOS equally well compared to higher number of \( k \)-points calculations.

E Electronic structure

The total electronic density of states (TDOS) at the equilibrium volume for all A–IRMOF-1 compounds investigated are displayed in Fig. 3. The partial density of states (PDOS) for the representative example A = Be in the A–IRMOF-1 series is shown in Fig. 2. The data for the remaining members of the series can be found in the ESI.<ref>

The bandgap (\( E_g \)) values obtained from the TDOS curves in Fig. 3 and Fig. S1–S4 (ESI<ref>) are summarized in Table 3. The bandgap values are ca. 3.5 eV for all members of the A–IRMOF-1 series. The values indicate that these materials are semiconductors, in agreement with previously reported LDA values of 3.4830–3.5045 eV.<ref> It can be seen that the characteristic peaks of TDOS for all these compounds are very similar which implies that the calculated bandgaps within the A–IRMOF-1 series have a common structural origin that is similar to IRMOF-1.

![Fig. 3 Calculated total density of states (TDOS) for A–IRMOF-1 (A = Be, Mg, Ca, Sr, Ba) in cubic Fm\( \overline{3}m \) symmetry (no. 225).](image)

<table>
<thead>
<tr>
<th>A–IRMOF-1</th>
<th>Theo. ( E_g ) eV</th>
<th>AO</th>
<th>Exp. ( E_g ) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be–IRMOF-1</td>
<td>3.487 (3.483&lt;ref&gt;)</td>
<td>BeO</td>
<td>10.9&lt;ref&gt;</td>
</tr>
<tr>
<td>Mg–IRMOF-1</td>
<td>3.579 (3.500&lt;ref&gt;)</td>
<td>MgO</td>
<td>7.2&lt;ref&gt;</td>
</tr>
<tr>
<td>Ca–IRMOF-1</td>
<td>3.534 (3.504&lt;ref&gt;)</td>
<td>CaO</td>
<td>6.2&lt;ref&gt;</td>
</tr>
<tr>
<td>Sr–IRMOF-1</td>
<td>3.481</td>
<td>SrO</td>
<td>5.3&lt;ref&gt;</td>
</tr>
<tr>
<td>Ba–IRMOF-1</td>
<td>3.238</td>
<td>BaO</td>
<td>4.0&lt;ref&gt;</td>
</tr>
<tr>
<td>IRMOF-1 (MOF-5)</td>
<td>3.4–3.5&lt;ref&gt;,&lt;ref&gt;</td>
<td>ZnO-w/-z&lt;ref&gt;</td>
<td>3.455/3.300&lt;ref&gt;</td>
</tr>
</tbody>
</table>

It is a very significant observation that the bandgap is unaffected by the identity of the cornerstone metal. By contrast, in a recent theoretical study, Choi et al.<ref> reported a tuning of electronic bandgaps from semiconducting to metallic states by substitution of Zn(II) ions in IRMOF-1 with Co(II) ions. The differences in how the electronic properties are affected by the two different kinds of metal replacement can be understood as follows. All the compounds in the A–IRMOF-1 series and IRMOF-1 have the same linkers and similar nodes. Although the alkaline earth metals in this series have different atomic numbers and atomic or ionic radii, they have the same valence shell electron configurations. The replacement of divalent Zn ions in IRMOF-1 with divalent alkaline-earth metal ions gives a similar electronic structure and bonding behavior. The iso-electronic nature of the compounds within this series contributes to the similar TDOS patterns and also the very similar bandgap values. In contrast, the transition metal ion Co(II) is very different from the main group alkaline earth metals, as this ion may have a valence state quite different from Zn(II) and the alkaline earth ions A(II). This can contribute to the tuning process of the bandgap of IRMOF-1 and its Co congener. Moreover, Co(II) ions often exhibit spontaneous magnetic ordering which will also contribute to metallic behavior. As Co has a different electronic configuration compared with alkaline-earth metals, the 3d electrons of Co should play an important role in the tuning process. We conclude that metal atoms with different electron configurations may be used to efficiently tune the electronic structure of IRMOF-1.
It should be noted that the bandgap values estimated from regular DFT calculations are generally smaller than those determined experimentally.\textsuperscript{29,30} Such an underestimation of the calculated bandgaps is an intrinsic feature of the \textit{ab initio} method and is related to the DFT limitations, namely not taking into account the discontinuity in the exchange-correlation potential.\textsuperscript{31} To overcome this discrepancy, the so-called scissor operator, \( \Delta \), can be introduced, which effectively eliminates the difference between the theoretical and experimental bandgap values by means of a simple rigid shift of the unoccupied conduction band with respect to the valence band.

In the following we will briefly discuss and compare theoretical and experimental bandgap values for IRMOF-1, and make comparisons with the calculated data for the hypothetical systems A–IRMOF-1 and their corresponding bulk binary oxides. As mentioned, calculated bandgap values for the A–IRMOF-1 systems investigated by us are almost constant, independent of the different cornerstone cations. In contrast, the experimental bandgap values for the binary oxides of the corresponding cations are quite different: in particular, they have much higher bandgap values than do the A–IRMOF-1 series. As the bandgap values of ZnO and MOF-5 are almost the same, this may cause the appearance of a one-to-one correspondence between the bandgap values of IRMOFs and those of the corresponding binary oxides. However, the above results suggest that there is no such simple relationship. MOFs are porous materials constructed from linkers and nodes and the bonding interactions in MOFs are quite different from those in close-packed oxides. The origin of bandgap formation in MOFs is different from that in binary oxides. Hence, one may not predict the properties of MOFs from the properties of the corresponding oxides that are involved in the formation of the MOF nodes. If detailed information about and understanding of electronic structures and chemical bonding in MOFs is desired, it is therefore advisable to perform \textit{ab initio} calculations.

\section*{F Chemical bonding analysis}

\subsection*{i From partial density of states.}

For simplicity, we use Be–IRMOF-1 as a representative example to analyze the partial density of states (PDOS) for the whole A–IRMOF-1 series. Data for the remaining members of the series may be taken into account the discontinuity in the exchange-correlation potential.\textsuperscript{31} To overcome this discrepancy, the so-called scissor operator, \( \Delta \), can be introduced, which effectively eliminates the difference between the theoretical and experimental bandgap values by means of a simple rigid shift of the unoccupied conduction band with respect to the valence band.

In the following we will briefly discuss and compare theoretical and experimental bandgap values for IRMOF-1, and make comparisons with the calculated data for the hypothetical systems A–IRMOF-1 and their corresponding bulk binary oxides. As mentioned, calculated bandgap values for the A–IRMOF-1 systems investigated by us are almost constant, independent of the different cornerstone cations. In contrast, the experimental bandgap values for the binary oxides of the corresponding cations are quite different: in particular, they have much higher bandgap values than do the A–IRMOF-1 series. As the bandgap values of ZnO and MOF-5 are almost the same, this may cause the appearance of a one-to-one correspondence between the bandgap values of IRMOFs and those of the corresponding binary oxides. However, the above results suggest that there is no such simple relationship. MOFs are porous materials constructed from linkers and nodes and the bonding interactions in MOFs are quite different from those in close-packed oxides. The origin of bandgap formation in MOFs is different from that in binary oxides. Hence, one may not predict the properties of MOFs from the properties of the corresponding oxides that are involved in the formation of the MOF nodes. If detailed information about and understanding of electronic structures and chemical bonding in MOFs is desired, it is therefore advisable to perform \textit{ab initio} calculations.

\subsection*{ii From charge density/transfer, ELF, and BOP analyses.}

In order to further improve the understanding of the bonding interactions, we turn our attention to charge densities and related quantities. The situation for A = Be is depicted in Fig. 4, and similar figures for the remaining A–IRMOF-1 series can be found in ESI\textsuperscript{f}. Fig. S5–S8. For Be–IRMOF-1, it is apparent that the charges are largely spherically distributed at the Be and O sites (Fig. 4a), which is the characteristic for systems having ionic interactions. Additionally, there is no substantial charge density distributed between the Be and O atoms, which also clearly demonstrates the presence of largely ionic bonding. However, the charge density plot shows a slight deviation from exact spherical distribution, indicative of a slight covalent character of the Be–O bonding. Importantly, compared with Be–IRMOF-1 the bonding interaction between alkaline-earth metal and oxygen is more ionic in Ba–IRMOF-1 (Fig. S8, ESI\textsuperscript{f}), as would be expected from the different electronegativities of the metals. It can be inferred that the ionic character of the A–O bond increases and its covalency decreases when one goes from Be to Ba in the series. These conclusions, arrived at from charge density analyses, are consistent with the following analyses based on charge transfer and ELF.

Charge transfer plots provide an alternative convenient and illustrative means to represent and analyze the bonding characteristics in solids. The charge-transfer contour is the difference between the self-consistent electron density in a particular plane, \( \rho_{\text{comp}} \), and the electron density of the
interaction for the constituents of a solid. 19–22 The ELF plot property that discriminates between different kinds of bonding Bader charge analysis and Mulliken population analysis. ionic–covalent bonding between Be and O, with a predominant charge transfer from Be to O sites indicates the presence of the bonding interaction between Be and O. The anisotropic transfer around the O sites indicates a covalent contribution to bonds. Additionally, the non-spherical distribution of charge indicative of the some covalent contribution to the Be–O bond. However, the charge Be–IRMOF-1 is given in Fig. 4b. It is apparent that electrons are transferred from Be to O sites. However, the charge transfer from Be is not isotropic to the extent indicated in Fig. 4a. There is a clear overlap between Be and O in Fig. 4b, indicative of the some covalent contribution to the Be–O bonds. Additionally, the non-spherical distribution of charge transfer around the O sites indicates a covalent contribution to the bonding interaction between Be and O. The anisotropic charge transfer from Be to O sites indicates the presence of ionic–covalent bonding between Be and O, with a predominant ionic interaction. This conclusion is supported by a following Bader charge analysis and Mulliken population analysis.

The electron localization function (ELF) is a ground-state property that discriminates between different kinds of bonding interaction for the constituents of a solid. 19–22 The ELF plot for Be–IRMOF-1 is given in Fig. 4c. In general, for Be, there are large values of ELF at the O sites, indicating strongly paired electrons with local bosonic character. The negligibly small ELF between Be and O, and the small values of ELF at the Be sites with nearly spherically symmetric distribution indicate that the bonding interaction between Be and O is mainly ionic. The ELF distribution at the O site is not spherically symmetric but rather is polarized towards the Be atom, indicative of noticeable directional bonding between Be and O. By comparing the ELF distribution in Be–IRMOF-1 with that in Ba–IRMOF-1 (Fig. 4e and Fig. S8c, ESI†), we infer that the ELF distribution at the Ba/O sites in Ba–IRMOF-1 are more spherically symmetric than that at the Be/O sites in Be–IRMOF-1. This again indicates that there is more ion contribution to the Ba–O bond than to the Be–O bond. Thus, the ionic character of the A–O bond increases when one goes from Be to Ba in the A–IRMOF-1 series. A certain polarized character is found in the ELF distribution at the H sites in A–IRMOF-1, indicating the presence of ionic–covalent bonding. There is a maximum in the ELF between C atoms, and between C and O atoms, indicative of covalent bonding. The ELF for the subunit O\(_2\)C–C\(_6\)H\(_4\)–CO\(_2\) is almost the same for the whole series indicating that the A ion replacement does not significantly influence the bonding character of this structural subunit. From the above analyses, one can clearly visualize mixed chemical bonding behavior in the A–IRMOF-1 series.

In order to provide further quantitative understanding about the interactions between the constituents, the bond overlap population (BOP) values were calculated on the basis of the Mulliken population analysis. 38 The Mulliken charge and bond overlap population data are useful for evaluating the covalent, ionic, or metallic nature of bonds in a compound. Positive and negative bond overlap population values indicate bonding and antibonding states, respectively. A BOP value close to zero indicates that there is no significant interaction between the electronic populations of the two atoms. 39 BOP values greater than zero indicate increasing levels of covalency. Also, a high value of the bond overlap population indicates a covalent bond, whilst a low value indicates an ionic nature. Although the physical meaning and scientific interpretation of the values of Mulliken charges or bond populations in metallic systems is not clear, the sign of bonding between atoms is unequivocal. 40

The calculated BOP values for the A–O, C–O, C–C, and C–H bonds are displayed in Table 4. Here, it can be seen that the BOP values for the A–O bonds in the MOF structures range from 0.36 to 0.37 (Be–O), 0.23 (Mg–O), 0.14–0.18 (Ca–O), 0.14–0.17 (Sr–O), and 0.11 to 0.16 (Ba–O). Analogously, the calculated BOP values for the C2–O2 bonds are 0.92 (Be), 0.91 (Mg), 0.89 (Ca), 0.89 (Sr), and 0.89 (Ba), values which are very close to that of a covalent C–O single bond. The BOP values for the C3–H bonds, ranging from 0.86 to 0.89, are rather insensitive to the nature of the metal A, underscoring the strongly covalent character of these bonds. For the C–C bonds, the calculated BOP values vary in the range 0.84–1.10 (Be), 0.84–1.11 (Mg), 0.82–1.09 (Ca), 0.81–1.09 (Sr), and 0.81–1.09 (Ba). The calculated BOP values for the benzene-ring C–C bonds are essentially identical at ca. 1.09, somewhat greater than for the benzene-ring–carboxylate C–C bonds at ca. 0.81. In general, these values are near those of the covalent C–C bond in diamond (1.08), and there is no doubt that the C–C bonds in these MOFs are strong covalent bonds.

The approximate order of the BOP values for A–O < C–H ≈ C–O < C–C. The A–O bonds in the nodes of A–IRMOF-1 have dominant ionic character, such as is found in the bulk
Table 4 Calculated Mulliken effective charges (MEC), bond overlap populations (BOP), and Bader charges (BC) for the A-IRMOF-1 (A = Be, Mg, Ca, Sr, Ba) series

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atom site</th>
<th>MEC (e)</th>
<th>BOP</th>
<th>BC (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be-IRMOF-1</td>
<td>H</td>
<td>+0.31</td>
<td>0.86 (H–C3)</td>
<td>+0.0663</td>
</tr>
<tr>
<td></td>
<td>C1</td>
<td>−0.61</td>
<td>0.84 (C1–C2)</td>
<td>+2.6603</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>−0.05</td>
<td>1.08 (C2–C3)</td>
<td>+0.0308</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>−0.26</td>
<td>1.10 (C1–C3)</td>
<td>−0.0040</td>
</tr>
<tr>
<td></td>
<td>O1</td>
<td>−0.96</td>
<td>0.37 (Be–O1)</td>
<td>−2.0065</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>−0.63</td>
<td>0.92 (C1–O2)</td>
<td>1.9073</td>
</tr>
<tr>
<td></td>
<td>Be</td>
<td>+1.14</td>
<td>0.36 (Be–O2)</td>
<td>+2.0000</td>
</tr>
<tr>
<td>Mg-IRMOF-1</td>
<td>H</td>
<td>+0.28</td>
<td>0.89 (H–C3)</td>
<td>+0.0700</td>
</tr>
<tr>
<td></td>
<td>C1</td>
<td>+0.60</td>
<td>0.84 (C1–C2)</td>
<td>+2.6679</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>−0.06</td>
<td>1.08 (C2–C3)</td>
<td>+0.0194</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>−0.26</td>
<td>1.11 (C1–C3)</td>
<td>−0.0908</td>
</tr>
<tr>
<td></td>
<td>O1</td>
<td>−1.28</td>
<td>0.23 (Mg–O1)</td>
<td>−1.9979</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>−0.71</td>
<td>0.91 (C1–O2)</td>
<td>−1.9040</td>
</tr>
<tr>
<td>Mg</td>
<td>+1.58</td>
<td>0.23 (Mg–O2)</td>
<td>+2.0000</td>
<td></td>
</tr>
<tr>
<td>Ca-IRMOF-1</td>
<td>H</td>
<td>+0.31</td>
<td>0.86 (H–C3)</td>
<td>+0.0677</td>
</tr>
<tr>
<td></td>
<td>C1</td>
<td>+0.66</td>
<td>0.82 (C1–C2)</td>
<td>+2.6690</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>−0.06</td>
<td>1.07 (C2–C3)</td>
<td>+0.0361</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>−0.27</td>
<td>1.09 (C1–C3)</td>
<td>−0.0216</td>
</tr>
<tr>
<td></td>
<td>O1</td>
<td>−1.14</td>
<td>0.18 (Ca–O1)</td>
<td>−1.5063</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>−0.70</td>
<td>0.89 (C1–O2)</td>
<td>−1.8127</td>
</tr>
<tr>
<td></td>
<td>Ca</td>
<td>+1.35</td>
<td>0.14 (Ca–O2)</td>
<td>+1.6185</td>
</tr>
<tr>
<td>Sr-IRMOF-1</td>
<td>H</td>
<td>+0.31</td>
<td>0.86 (H–C3)</td>
<td>+0.0498</td>
</tr>
<tr>
<td></td>
<td>C1</td>
<td>+0.64</td>
<td>0.81 (C1–C2)</td>
<td>+2.6918</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>−0.06</td>
<td>1.08 (C2–C3)</td>
<td>+0.0224</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>−0.27</td>
<td>1.09 (C1–C3)</td>
<td>−0.0058</td>
</tr>
<tr>
<td></td>
<td>Sr</td>
<td>+1.14</td>
<td>0.17 (Sr–O1)</td>
<td>−1.4561</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>−0.70</td>
<td>0.89 (C1–O2)</td>
<td>−1.8161</td>
</tr>
<tr>
<td></td>
<td>Sr</td>
<td>+1.39</td>
<td>0.14 (Sr–O2)</td>
<td>+1.6092</td>
</tr>
<tr>
<td>Ba-IRMOF-1</td>
<td>H</td>
<td>+0.30</td>
<td>0.86 (H–C3)</td>
<td>+0.0576</td>
</tr>
<tr>
<td></td>
<td>C1</td>
<td>+0.64</td>
<td>0.81 (C1–C2)</td>
<td>+2.7187</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>−0.06</td>
<td>1.08 (C2–C3)</td>
<td>+0.0013</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>−0.27</td>
<td>1.09 (C1–C3)</td>
<td>−0.0203</td>
</tr>
<tr>
<td></td>
<td>O1</td>
<td>−1.08</td>
<td>0.16 (Ba–O1)</td>
<td>−1.4287</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>−0.69</td>
<td>0.89 (C1–O2)</td>
<td>−1.8185</td>
</tr>
<tr>
<td>Ba</td>
<td>+1.36</td>
<td>0.11 (Ba–O2)</td>
<td>+1.6207</td>
<td></td>
</tr>
</tbody>
</table>

oxides AO, whereas the C–H, C–O and C–C bonds in the linkers of A–IRMOF-1 have covalent interactions such as found in ordinary organic molecules.

In order to further supplement the understanding of the bonding interactions related to charge transfer between the atoms it is useful to identify the exact number of electrons at a particular atom in a molecule or a group of atoms in a solid, it has nevertheless proved useful in many cases to perform population analyses. Due to its simplicity, the Mulliken population scheme has become the most popular approach. This method is more qualitative than quantitative, and provides results that are sensitive to the atomic basis. The calculated Mulliken effective charges (MEC, Table 4) for A-IRMOF-1 range +0.28 to +0.31 |e| in the series, as are the MEC values on corresponding C-atoms (C3 −0.26 to −0.27 |e|, C1 +0.60 to +0.66 |e|, C2 −0.05 to −0.06 |e|). This indicates negligible effects of metal substitution on the charge distributions in the organic linkers.

Finally, the bonding and electron distribution was subjected to a Bader topological analysis. Although there is no unique way to identify how many electrons are associated with an atom in a molecule or an atomic group in a solid, in addition to the Mulliken analysis above it has also proved useful in many cases to perform Bader analyses. In the Bader charge (BC) analysis, each atom of a compound is surrounded by a surface (called a Bader region) that runs through minima of the charge density, and the total charge of an atom is determined by integration of electrons within the Bader region. Using this approach the calculated Bader charges for the A-IRMOF-1 series are given in Table 4. The BC for A and O in the A-IRMOF-1 compounds indicate that the interaction between A and O is almost ionic. In all cases nearly two electrons (2.00, 2.00, 1.62, 1.61, and 1.62 for A = Be, Mg, Ca, Sr, and Ba, respectively) are transferred from A to O. This finding is consistent with the DOS and charge density analyses.

Within the A2O units, Ba donates nearly 1.8 electrons in Ba-IRMOF-1, Be donates nearly 1.2 electrons in Be-IRMOF-1, which is much smaller than in a pure ionic picture. This is associated with the noticeable covalency present between Be/Ba and O as already demonstrated. The covalency of the Be–O bond is greater than that of the Ba–O bond and hence Ba donates as much as 0.6 electrons more than Be. However, this conclusion may be due to the artifact of making boundaries to integrate charges in each atomic basin using Bader’s “atoms in molecule” approach. Anyway, the results from the BC analysis are consistent with the charge density, charge transfer, ELF, and PDOS analysis, i.e. A atoms donate electrons to the O sites.

In order to clearly visualize the essential calculated quantities concerning charge distribution and chemical bonding in the A-IRMOF-1 series, Fig. S9 (ESI) depicts all calculated Bader charges (BC), bond overlap populations (BOP), and Mulliken effective charges (MEC) for the whole A-IRMOF-1 series (A = Be, Mg, Ca, Sr, and Ba) for an at-a-glance assessment.

In summary, although different formalisms are used and some small differences are seen between data arising from different analysis tools, the qualitative conclusions that are drawn from electronic charge density, charge transfer, ELF, Bader charge, Mulliken population, and PDOS analyses are highly consistent. The chemical bonding picture for the whole A-IRMOF-1 series is therefore quite clear and unequivocal.

G Band structure and optical properties

Studies of the optical properties for the A-IRMOF-1 series are important in view of their potential uses in hybrid solar cell applications as an active material or in the buffer layer between the electrodes and inorganic active materials. Furthermore, optical properties studies are of fundamental interest, since optical transitions involve not only the occupied and unoccupied parts of the electronic structure, but also carry information about the character of the bands. This is also
related to the excited-state properties of A–IRMOF-1 series, which may be important for certain applications.

The central quantity of the optical properties is the optical dielectric function $\varepsilon(\omega)$, which describes the features of linear response of the system to an electromagnetic radiation, which again governs the propagation behavior of radiation in a medium. Here $\varepsilon(\omega)$ is connected with the interaction of photons with electrons. Its imaginary part $\varepsilon_2(\omega)$ can be derived from interband optical transitions by calculating the momentum matrix elements between the occupied and unoccupied wave functions within the selection rules, and its real part $\varepsilon_1(\omega)$ can be derived from $\varepsilon_2(\omega)$ by the Kramer–Kronig relationship. The real part of $\varepsilon(\omega)$ in the limit of zero energy (or infinite wavelength) is equal to the square of the refractive index $n$. All the frequency dependent linear optical properties such as refractive index $n(\omega)$, absorption coefficient $\alpha(\omega)$, reflectivity $R(\omega)$, optical conductivity $\sigma(\omega)$, and electron energy-loss spectrum $L(\omega)$ can be deduced from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.

We have now performed CASTEP calculations to estimate the optical properties and band structures for the whole A–IRMOF-1 series. The results for A = Be are shown in Fig. 5 and 6. The optical properties and band structures for the remaining members of this series can be found in the ESI†, Fig. S10–S17. The brief description and discussion will focus on A = Be and, to some extent, on Ba as the other extreme member of the series.

The dielectric function of Be–IRMOF-1 (Fig. 5a) allows us to estimate the value of the refractive index at an infinite wavelength of about 1.279. There are four peaks at 4.81, 6.04, 8.37 and 14.63 eV in the imaginary part of a dielectric function $\varepsilon_2(\omega)$ plot. In comparison, the estimated value of the refractive index at infinite wavelength is $\approx 1.205$ for A = Ba, slightly smaller than for Be. Moreover, there are many more peaks in the $\varepsilon_2(\omega)$ spectrum for A = Ba (Fig. S16a, ESI†), many of which are quite broad. However, six relatively distinct peaks at 4.93, 6.23, 8.63, 13.83, 29.78, and 31.16 eV are identified in $\varepsilon_2(\omega)$. At low frequencies (0–3.5 eV) the imaginary part of the

---

**Fig. 5**  Calculated optical spectra for Be–IRMOF-1: (a) dielectric function $\varepsilon(\omega)$; (b) reflectivity $R(\omega)$; (c) refractive index $n(\omega)$ and extinction coefficient $k(\omega)$; (d) optical conductivity $\sigma(\omega)$; (e) energy loss function $L(\omega)$; (f) absorption coefficient $\alpha(\omega)$ (cm$^{-1}$).
optical dielectric function \( \varepsilon_2(\omega) \) approaches zero for all members of the series, which is consistent with the bandgap of the A–IRMOF-1 series.

The reflectivity spectrum \( R(\omega) \) of Be–IRMOF-1 (Fig. 5b) exhibits two major peaks at 4.51 and 14.92 eV. The peak at 4.51 eV mainly arises from the Be/H (s) → C/O (2p) interband transition. In contrast, for Ba–IRMOF-1 (Fig. S16a, ESI†) there are many more, and mostly more diffuse, peaks in the reflectivity spectrum \( R(\omega) \) compared with that in the Be analogue. Three major peaks are located at 4.59, 13.83, and 31.71 eV. The peak at 4.59 eV for Ba–IRMOF-1 mainly arises from the H (1s) → C/O (2p) interband transition.

The extinction coefficient \( k(\omega) \), or the imaginary part of the complex refractive index, of Be–IRMOF-1 (Fig. 5c) shows five peaks at 4.95, 6.18, 8.45, 14.92 and 17.61 eV. Again, there are many more, and more diffuse, in the extinction coefficient \( k(\omega) \) plot of Ba–IRMOF-1 (Fig. S16c, ESI†). Relatively well-defined peaks are seen at 5.08, 6.31, 14.04 and 29.78 eV.

The optical conductivity \( \sigma(\omega) \) plot of Be–IRMOF-1 is shown in Fig. 5d. The real part of the complex conductivity, \( R e(\sigma) \), has five peaks at 4.88, 6.18, 8.48, 14.70 and 17.46 eV. There are many more peaks in the \( R e(\sigma) \) plot for Ba–IRMOF-1 (Fig. S16d, ESI†). In fact, as many as twelve peaks are discernible from 5.14 to 31.09 eV in \( R e(\sigma) \) for Ba.

The electron energy-loss function \( L(\omega) \) (Fig. 5e) is an important optical parameter describing the energy loss of a fast electron traversing in a certain material. The peaks in the \( L(\omega) \) spectra represent the characteristics associated with the plasma resonance and the corresponding frequency is the so-called screened plasma frequency above which the material is dielectric \( [\varepsilon(\omega) > 0] \) and below which the material behaves like a metallic compound in some sense \( [\varepsilon(\omega) < 0] \). In addition, the peaks of the \( L(\omega) \) spectra overlap the trailing edges in the reflectivity spectra. One group of peaks of \( L(\omega) \) of Be–IRMOF-1 is located at 5.24 and 6.48 eV (which corresponds to the reduction of \( R(\omega) \)), and a second group includes more intense peaks at 15.94 and 18.41 eV which tails off to ca. 40 eV. The main features of \( L(\omega) \) for A = Ba are quite different from those for Be. Most notably, there are many more peaks and complexity in \( L(\omega) \) for Ba (Fig. S16e, ESI†). Here, the plasma resonance peaks may be separated into four groups. In the first group, the major peak is at 6.58 eV. The second is centered at 16.38 eV. The third group comprises rather faint peaks around 25 eV, and in the fourth group there are two distinct peaks at 30.06 and 31.29 eV.

Be–IRMOF-1 has an absorption band \( \alpha(\omega) \) (Fig. 5f) that ranges from 3.5 to 50.6 eV with five peaks at 5.03, 6.26, 8.51, 15.00, and 17.68 eV before it tails off at ca. 50 eV. The most distinct peak is the one at 17.68 eV. By comparison, the absorption band \( \alpha(\omega) \) for Ba–IRMOF-1 (Fig. S16f, ESI†) has many more peaks and a greater complexity than that of Be–IRMOF-1. The absorption band for the Ba system ranges from 3.5 to 47.8 eV, which again contains four groups of peaks. In the first, there is a major peak at 6.44 eV. The second group has its main peak at 16.16 eV. The third group has three rather faint peaks around 25 eV and finally, two closely separated sharp peaks are seen in the fourth group at 29.86 and 31.16 eV. In descriptive terms, the shape of \( \alpha(\omega) \) for A = Ba is somewhat similar to that of \( L(\omega) \) for A = Ba.

Analogously, it is also seen that the shape of the \( \alpha(\omega) \) plot for A = Be is somewhat similar to that of \( L(\omega) \) for A = Ba.

In general, the number of peaks in the optical spectra increases when one goes from A = Be to Ba. Moreover, the peaks become broader and the spectra gain complexity when one goes through the series from A = Be to Ba.

In conjunction with the optical properties calculations we have also calculated the band structures of the whole A–IRMOF-1 series. The results for A = Be are shown in Fig. 6, and the remaining members of series are included in the ESI†. For the high symmetry directions in the Brillouin zone sampling, CASTEP automatically chose the \( W - L - \Gamma - X - W - K \) path for the FCC symmetry Brillouin zone. Fig. 6 clearly shows that the bands in the valence band as well as in the conduction band are almost parallel and dispersionless. The bands at the VB maximum and CB minimum for all investigated A–IRMOF-1 members are flat, and this is a common feature for these MOF materials. This flat band behavior makes it impossible to unequivocally identify whether the band gap is direct or indirect. However, we still can gain some qualitative information from the band structures that helps to understand the electronic structures of MOF materials and provides further insight into their optical properties.

Even though the investigated A–IRMOF-1 systems are isoelectronic and isstructural, with nearly the same bandgap values, their band structures have noticeable differences in both the VB and the CB. This can be illustrated when the extreme members Be (Fig. 6) and Ba (Fig. S17, ESI†) are
compared. The bands in the VB structure of the Ba system are considerably narrower, and their distribution is well isolated, compared to the VB structure of the Be system. This isolated band feature in the Ba system is also reflected in DOS, in that there are well isolated peaks in the total DOS of the Ba system compared to that of the Be system. The well isolated band feature in the Ba case is associated with the strong ionic bonding between Ba and the host lattice and also with its greater equilibrium volume due to the larger cation radius of Ba, which reduces overlap interaction between atoms. The more noticeable covalent bonding between Be and the host lattice, as well as the smaller equilibrium volume of the Be system, cause more extensive overlap interactions between the constituents. This increase in overlap interaction is the origin of the increased band dispersion in $A = Be$ compared to the other compounds considered in the A–IRMOF-1 series.

IV. Conclusions

A detailed computational investigation on the electronic structure, chemical bonding, formation energies, and optical properties of the A–IRMOF-1 ($A = Be, Mg, Ca, Sr, Ba$) series using first-principles methods has been presented. The following important conclusions have been reached.

1) The calculations show that the A–IRMOF-1 series can be stable in the cubic crystal structure. The lattice parameters, bulk moduli, bond lengths and bond angles obtained from our structural optimization are in good agreement with previous theoretical results, when available. The equilibrium structural parameters for $A = Sr$ and $Ba$ are predicted for the first time. Our comprehensive structural data for the A–IRMOF-1 series should be useful for experimentalists to characterize new materials and to compare with future experimental or computational studies.

2) The estimated values for formation enthalpies suggest that it should be possible to synthesize all the compounds in this A–IRMOF-1 ($A = Be, Mg, Ca, Sr, Ba$) series since their formation energies are more negative than that of the well-known stable compound IRMOF-1 (MOF-5).

3) The analyses of calculated charge density, charge transfer, ELF, Bader charge and Mulliken population reveal the nature of the A–O, O–C, H–C and C–C bonds, i.e., A–O bonds have mainly ionic character with noticeable covalency and ionocities that depend on the identity of A. The O–C, H–C and C–C bonds are as expected mainly of covalent character.

4) Electronic density of states (DOS) studies show that the A–IRMOF-1 compounds have a band gap of ca. 3.5 eV, resulting in semiconductor behavior. Interestingly, the bandgap values do not change much with changes in the A cation.

5) The optimized structural parameters and calculated DOS do not change very much with the number of $k$-points involved in the calculation. This indicates the great potential of computational modeling of even more complex MOFs, suggesting the possibility to model MOF systems with large number of atoms using less demanding computational resources.

6) The calculated optical properties of the A–IRMOF-1 series provide useful information for the future experimental exploration and indicate their potential for applications in optoelectronic devices, especially in solar cells.

Acknowledgements

The authors gratefully acknowledge the Research Council of Norway for financial support and for the computer time at the Norwegian supercomputer facilities.

References