Ab initio electronic structures of rhombohedral and cubic HgXO$_3$ (X = Ti, Pb)

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Abstract
First-principles calculations were performed for orthorhombic HgO, rhombohedral and cubic
phases of HgTiO$_3$ (HTO) and HgPbO$_3$ (HPO). The calculations show that in the rhombohedral
phase HTO is a direct gap insulator with a gap of ∼1.6 eV. The rhombohedral phase of HPO, on
the other hand, shows a weak metallic character. The results provide an explanation for the
electrical properties of these compounds. The cubic phases of HTO and HPO are invariably
metallic in nature, thereby suggesting that for HTO the rhombohedral–cubic transition must
also be accompanied by a change in the electrical state. Examination of the electronic density of
states of these systems revealed no significant on-site mixing of Hg 5d and Hg 6s states in any
of these materials.

1. Introduction

Oxides of mercury are known to exhibit interesting crystal chemistry due to the unusual bonding characteristic of mercury. The simplest oxide HgO possesses an orthorhombic structure at room temperature which, on heating above 220 °C, transforms to a hexagonal phase [1]. Both phases are based on zigzag –Hg–O–Hg–O– chains. Conventionally, it has been accepted that a linear coordination environment of Hg promotes intra-atomic mixing between the filled shallow core Hg 5d states and the nominally empty Hg 6s states, thereby lowering the electrostatic energy of the Hg^{+2} ions through a second-order Jahn–Teller effect [2]. As a result, despite its large size, Hg exhibits a preference for linear coordination, i.e. it has the tendency to form only two strong bonds with oxygen. For example, in HgO there are two Hg–O bonds at 2.03 Å and the other Hg–O distances are ∼2.9 Å [3]. This aspect of Hg coordination is also manifested in some other compounds such as Hg$_2$Nb$_2$O$_7$, Hg$_2$Ta$_2$O$_7$, Hg$_2$Sb$_2$O$_7$, HgWO$_4$, HgMoO$_4$ [4–7]. In contrast to this, HgTiO$_3$ (HTO) and HgPbO$_3$ (HPO) are ternary oxides in which Hg is known to exhibit a coordination of three. Both these compounds can, however, be synthesized only under high pressure conditions [8, 9]. HTO and HPO exhibit a rhombohedral structure (space group $R\bar{3}c$) at room temperature. A weak

dielectric anomaly has also been reported at 510 K [9] leading to the speculation that HTO may also be ferroelectric at room temperature. This, however, remains a speculation since the centrosymmetric structure, reported for HTO at room temperature, is not consistent with a global ferroelectric distortion in HTO. The analogous compound HgPbO$_3$ may be treated as part of the family of APbO$_3$ type compounds with A = Ba, Sr, Ca, Cd, etc [10–12]. Bi-modification of BaPbO$_3$, i.e. BaPb$_{1-x}$Bi$_x$O$_3$, is known to stabilize a superconducting state at low temperatures [13]. The Ba, Sr and Ca variants exhibit orthorhombic symmetry at room temperature. Of these BaPbO$_3$ and SrPbO$_3$ show metallic conductivity, presumably due to overlapping of Pb 6s (conduction band) and O 2p (valence band) states at the Fermi level [14]. In this paper we report the results of a first-principles study of HgPbO$_3$, and a closely related compound HgTiO$_3$ to understand their respective bonding characteristics and electronic structures.

2. Computational details

The calculations were performed using the Wien2k [15] implementation of the full-potential linearized augmented-plane-wave (FP-LAPW) method. The exchange–correlation potential is described by the generalized gradient approxima-

tion (GGA) of Perdew *et al* [16]. For HTO, HPO and HgO
the muffin-tin radii (RMT) of Hg, Pb, Ti and O were fixed
at 2.3, 2.3, 1.5 and 1.3 Bohr, respectively. Inside the muffin
tins wavefunctions were expanded in spherical harmonics up
to $l_{max} = 10$ and non-spherical contributions to the electron
density and potential up to $l_{max}^{pot} = 6$ was used. The energy
cutoff for the plane wave representation in the interstitial was
$E_{max} = 21.3$ Ryd for the wavefunctions, and $E_{pot._max} =
196$ Ryd for the potential. The total number of k-points in the
irreducible part of the Brillouin zone was kept at 56 for cubic
HTO/HPO, 32 for the rhombohedral structure of HTO/HPO
and 45 for orthorhombic HgO.

The structural parameters of HgTiO$_3$ were adopted from
those reported in [8]. The asymmetric unit of the rhombohedral
($R\bar{3}c$) structure consists of one Hg at $(0, 0, 1/4)$; one Ti at
$(0, 0, 0)$ and one oxygen (O) at $(0.4157, 0, 1/4)$. The lattice
parameters in the hexagonal setting are $a = 5.3781$ Å and
$c = 13.604$ Å. The hexagonal cell has six formula units of
HTO. The structure therefore has only three variables: the
x-coordinate of O and two lattice parameters. For HPO,
though the lattice parameters are known ($a = 5.7515$ Å and
$c = 14.534$ Å), the oxygen coordinate is not available in the
literature. In the present calculation we have assumed that this
coordinate in HPO is the same as in HTO.

3. Results and discussion

3.1. Energy–volume relationships

The total energy as a function of cell volume of the
rhombohedral HTO and HPO was calculated. The volume
was changed in a way that it preserves the c/a ratio
of the hexagonal cell. The equilibrium rhombohedral
volumes of HTO and HPO were obtained as 116 Å^3 and
146 Å^3, respectively. When compared with their respective
experimental values (114 Å^3 for HTO and 139 Å^3 for HPO),
the theoretical volume is larger by ∼2% for HTO and ∼5%
for HPO. These differences are within the acceptable limit of
uncertainty of this computational approach. Bulk modulus, B_0,
and its pressure derivative, B_0', were obtained by fitting the
Murnaghan equation of state [17, 18]:

$$E(V) = E_0 + \frac{B_0 V}{B_0'} \left(\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1 \right) - \frac{B_0 V_0}{B_0' - 1} \quad (1)$$

to the calculated E–V curve. B_0 and B_0' were found to be
177.9 GPa and 4.1, respectively, for HTO and 110.8 GPa
and 5.0, respectively, for HPO. Corresponding values from
experiments are lacking so far. Table 1 lists the relevant
parameters obtained in this study.

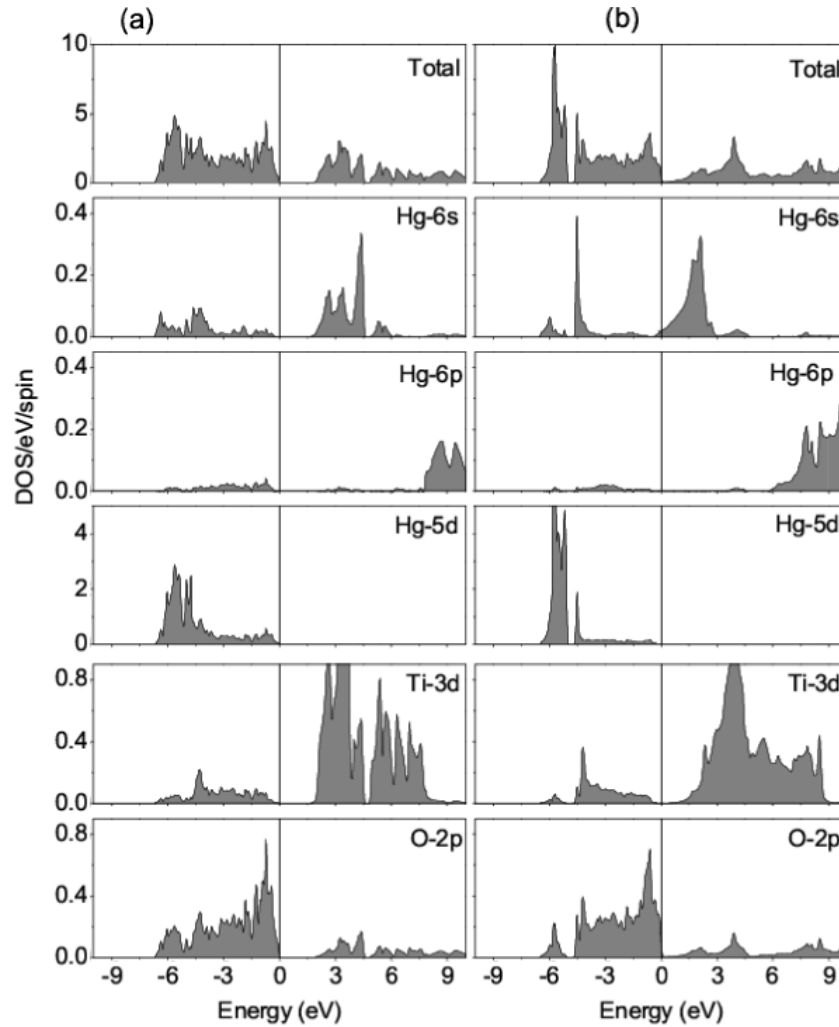### 3.2. Density of states of HgTiO$_3$ and HgO

Figure 1(a) shows the total and partial density of states of
the rhombohedral HTO calculated at the equilibrium lattice
parameters (see table 1). The valence band of HTO starts
close to the Fermi level down to −6.5 eV. The conduction
band, on the other hand starts at ∼1.6 eV above the Fermi

Table 1. Parameters of the rhombohedral phase of HgPbO$_3$ and
HgTiO$_3$ obtained from first-principles.

	Lattice parameters (Å)		Bulk modulus (GPa)	Electrical state
	Expt. [8]	Theor.		
HgTiO$_3$	$a = 5.38$	$a = 5.42$	178	Insulator (band gap ∼1.6 eV)
	$c = 13.61$	$c = 13.69$		
HgPbO$_3$	$a = 5.75$	$a = 5.85$	111	Metallic
	$c = 14.53$	$c = 14.78$		

level. Rhombohedral HTO is therefore an insulator with a
band gap of 1.6 eV. The calculated band structure revealed that
this gap occurs at the center of the Brillouin zone and hence
HTO is a direct band gap material. The predicted insulating
behavior is in conformity with the reported dielectric nature of
this compound [8, 9]. The valence band is constituted by the
O 2p and the shallow core Hg 5d states. The presence of the
Ti 3d states in the valence band is due to the hybridization of
these states with the O 2p states, a feature common to titanates.
Occurrence of noticeable Hg 6s states in the energy range −6.5
to −3.5, which is the energy range corresponding to the Hg 5d
states, suggests the presence of Hg 5d character in the Hg 6s
states.

The conduction band is primarily constituted by Ti 3d
and Hg 6s states in the range up to 8 eV and by Hg 6p at
higher energies. A noticeable presence of O 2p character
in the Hg 5d between the Fermi level and −5 eV and the
Hg 5d character in the O 2p states in the energy range −5
to −6.5 eV is suggestive of mixing between Hg 5d and O 2p
states. The mediation of O 2p states, instead of a direct on-site
mixing between the Hg 5d and 6s states, therefore seems to be
primarily responsible for bringing about the Hg 5d character
to the Hg 6s states in the valence band of rhombohedral HTO.
The absence of the Hg 6s character in the energy range 1.9–
4.5 eV in the unoccupied states of Hg 5d further supports this
argument. It may be mentioned that a similar intermixing of
O 2p with Hg 5d, Hg 6s and Hg 6p states was reported earlier
for the orthorhombic phase of HgO [19]. For the sake of direct
comparison we have also computed the electronic structure of
the orthorhombic phase of HgO using the relaxed structural
parameters given in [19]. The density of states of HgO, shown
in figure 2, reproduces the essential features of DOS of this
compound reported earlier [19]. A comparison of the Hg 6s
and Hg 6p PDOS of HTO and HgO suggests that there is
a stronger admixing of the Hg 6s states in the valence band
of HgO compared to that in HTO. Further, the maximum of
the Hg 6s PDOS occurs between −2.5 and −3.5 eV. This
energy range corresponds to a part of the O 2p states in the
valence band. The Hg 5d occupied states lie between −4.5
and −7.2 eV, i.e. ∼1 eV below the bottom of the Hg 6s PDOS
maximum. This implies that Hg 6s states in HgO have O 2p
character instead of the Hg 5d character. The occupied Hg 5d
states also have significant O 2p character as can be seen from
the Hg-PDOS plot of figure 2. Hence similar to the case of
rhombohedral HTO, the presence of Hg 5d character in the
occupied Hg 6s states of HgO is not primarily due to the on-
site mixing between both the states, as has been argued in the

Figure 1. Partial (PDOS) and total density of states (DOS) of HgTiO₃ for (a) rhombohedral and (b) cubic phases.

traditional literature [2], but is instead mediated by the O 2p states.

Electronic structure calculations were also performed for a cubic perovskite structure of HTO. The lattice parameter of the cubic structure was chosen so as to preserve the volume per formula unit of the rhombohedral structure. The DOS plots of the cubic HTO are shown in figure 1(b). It was found that the bottom of the conduction band and the top of the valence band meet near the Fermi level. The finite density of states at the Fermi level suggests that the cubic phase is metallic in nature. Shan *et al* [9] have shown that HTO does undergo rhombohedral–cubic transition at high pressures. However, so far no conductivity data as a function of pressure is available in the literature to verify this prediction. The valence band of the cubic HTO is formed by O 2p states down to −4.5 eV below the Fermi energy and by the Hg 5d states further below. The bottom of the conduction band corresponds to the tail of the Hg 6s states. The higher energy unoccupied states are formed by Ti 3d and Hg 6p states as in the rhombohedral HTO. The absence of the Hg 6p states in the valence band region is similar to what is observed for the rhombohedral case, suggesting insignificant mixing of this state with O 2p. The

most marked contrast between the electronic structures of the cubic and the rhombohedral structures of HTO is seen in the PDOS of the Hg 6s. The PDOS of Hg 6s shows a narrow peak at ∼−4.5 eV. Similar narrow peaks, in the same energy interval, can be seen in the PDOS of Hg 5d and O 2p. This band is more pronounced in the Hg 5d DOS thereby indicating that the narrow peak at −4.5 eV in the Hg 6s PDOS has Hg 5d character. Since the coordination of Hg is 12 in the cubic phase of HTO, the on-site mixing of Hg 6s and Hg 5d states, traditionally accepted for explaining the linear coordination of the Hg in Hg-compounds is of no relevance for the cubic case. Similar to the rhombohedral case, the absence of the Hg 6s character in the unoccupied states of Hg 5d confirms the insignificant on-site mixing of Hg 6s and Hg 5d states in both the rhombohedral and the cubic phases of HTO. On the other hand, the presence of Hg 5d character in the O 2p near −5 eV and vice versa for energies above −5 eV clearly suggests a hybridization of the Hg 5d and O 2p states. The Hg 5d character in the Hg 6s valence states therefore seems to be mediated by O 2p states.
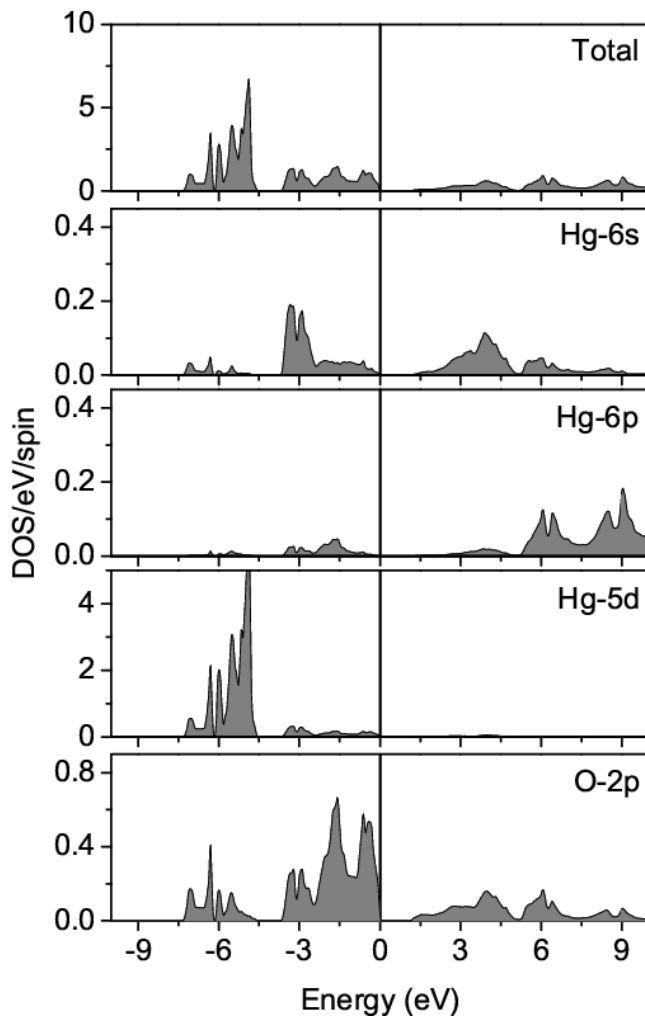
Figure 2. Partial and total density of states of the orthorhombic phase of HgO.

3.3. Density of states of HgPbO₃

Figure 3 shows the density of states of HgPbO₃ for the rhombohedral and cubic perovskite structures. The valence band is constituted by O 2p states down to −3.7 eV below the Fermi level, a strong narrow Hg 5d band centered at ∼−5 eV, and a broad weak Pb 6s band centered around −7 eV. The conduction band is formed by a narrow Hg 6s band centered at 2.8 eV above the Fermi level, followed by Pb 6s (2.3–5.5 eV) and Pb 6p states at higher energies (above 6.5 eV). It was noted that the top of the valence band and the bottom of the conduction band meet at the Fermi level at a small but finite density of states for the rhombohedral HPO. This suggests that, contrary to the rhombohedral HTO, rhombohedral HPO is an electrically conducting material. This is in agreement with the small resistivity (∼10^{-3} Ω cm) of HPO reported by Sleight *et al* [8]. A marked difference between the DOS of HTO and HPO is the narrowing of the Hg 5d band in the latter compound. The presence of the Hg 5d character in the valence band region of Hg 6s PDOS is similar to the HTO cases reported above. Also, the presence of Pb 6s and Hg 6s character in the O 2p PDOS both below and above the Fermi

level suggests the mixing of Pb 6s and Hg 6s with O 2p states. The O 2p character is also observed in the PDOS of Pb 6p and Pb 5d states. In the ionic limit, one would expect the Pb 6s and 6p states to be empty in the valence band region. Their presence, however, along with the Pb 5d, which otherwise lies well below 10 eV, suggests a strong covalent nature of the Pb–O bonds in HPO. This is not surprising in view of the six relatively short Pb–O distances (∼2.1 Å) as compared to the three Hg–O distances of ∼2.4 Å in the rhombohedral phase of HPO.

The essential features of the electronic structure in the cubic perovskite phase of HPO remain nearly the same as in the rhombohedral HPO. This phase is also conducting, as evident from the continuity of the valence and the conduction bands through the Fermi level (see the top panel of figure 3(b)). The relatively large DOS at the Fermi level in the cubic phase suggests that the conductivity of this phase will be better than its corresponding rhombohedral counterpart. Unlike the previous cases, the Hg 5d band in the cubic phase of HPO has become very narrow (peaked at −5.2 eV). As a result, the occupied Hg 6s PDOS has significantly reduced Hg 5d character. One reason that has led to this situation is the increase in the shortest Hg–O distances from 2.4 Å in the rhombohedral phase (Hg with three coordination) to 2.9 Å in the cubic phase (Hg with 12 coordination); the Pb–O distances in both the structures remain nearly unchanged at ∼2.1 Å. It may be reiterated that our calculations for the cubic phases of both systems, HTO and HPO, were carried out using cubic lattice parameters which would give the same volume per formula unit as the corresponding rhombohedral structure. There is no basis for this assumption though, and it was simply assumed for the sake of tentative comparison with the corresponding rhombohedral cases. Since a transition to a high symmetry cubic phase of a non-cubic structure, if any, is normally expected to happen at high pressures, in reality the volume per formula unit of the cubic phase should be smaller than its non-cubic parent phase. The present results show that even if the specific volume is kept unchanged the cubic phase becomes conducting for HTO; and the conductivity of the rhombohedral HPO increases in the cubic phase. This conclusion would remain valid since normal compounds are expected to show an increase in the electrical conduction with pressure.

4. Conclusions

First-principles calculations of the electronic structures of HgTiO₃ and HgPbO₃ revealed that HgTiO₃ is an insulator in the rhombohedral phase with a band gap of ∼1.6 eV. The HgPbO₃, on the other hand, is conducting in nature. The theoretical predictions are therefore consistent with the electronic behavior of these compounds reported in the literature. Examination of the density of states shows that while the top region of valence bands in both the cases are formed by O 2p states (as also in HgO) the bottom region of the conduction band is formed by Ti 3d states in HgTiO₃ and Pb 6s states in HgPbO₃. Both the compounds show mixing of the Hg 5d and Hg 6s states with the O 2p states. The on-site mixing of Hg 5d and Hg 6s states, if any, is not very significant in HgO
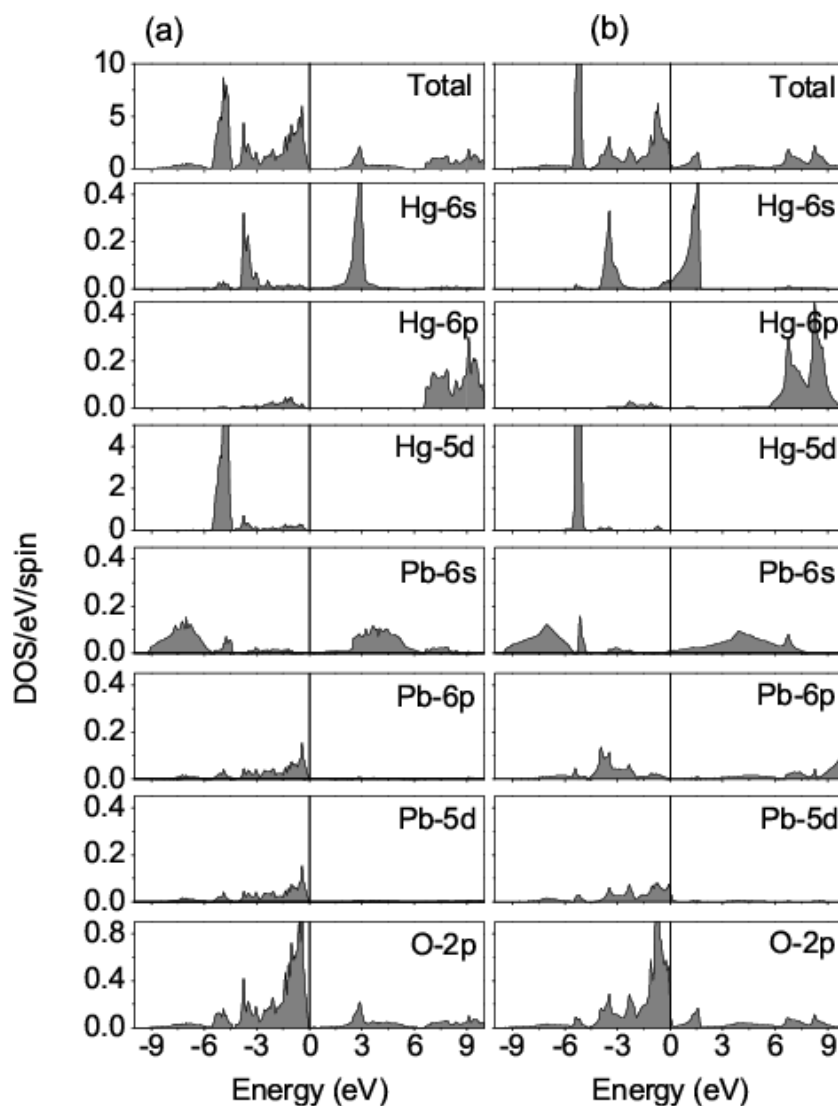
Figure 3. Partial (PDOS) and total density of states (DOS) of HgPbO₃ for (a) rhombohedral and (b) cubic phases.

and even less in HTO and HPO. The partial Hg 5d character of the Hg 6s states in the latter compounds is mediated by O 2p states. The cubic phases of HTO and HPO are conducting in nature.

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