

Structure of Cu_6PbO_8

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First-principles quantum mechanical calculations based on density functional theory were performed for Cu_6PbO_8 , hexacopper lead octaoxide, murdochite. The computed lattice parameter, density and bond lengths at ambient pressure are in good agreement with experimental data for murdochite. At about 18 GPa a phase transition is predicted, when a polymorph with a Suzuki-type structure, *i.e.* a close-packed structure with ordered vacancies, is proposed to become stable. The pressure dependence of the structural parameters has been calculated for the two polymorphs and their bulk moduli have been predicted. It is argued that the incorporation of halogen atoms is not a precondition for the stability of murdochite.

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1. Introduction

The crystal structure of Cu_6PbO_8 was first described by Christ & Clark (1955). They studied a natural sample of the then newly discovered rare mineral murdochite (Fahey, 1955) with the approximate composition $\text{Cu}_{6.1}\text{Pb}_{0.9}\text{O}_{8.0}$. Christ & Clark (1955) proposed a new simple cubic structure type for Cu_6PbO_8 . This suggested structure is closely related to the NaCl structure with a high content of ordered vacancies, so that its formula might be written as $\text{Cu}_6\text{Pb}\square\text{O}_8$, where \square denotes a vacancy. This structure may be envisaged as being composed of alternately stacked CuO and $\text{Cu}_{0.5}\text{Pb}_{0.25}\square_{0.25}\text{O}$ layers (Fig. 1). At about the same time it was suggested that Mg_6MnO_8 also crystallizes in the ' Cu_6PbO_8 structure' (Kasper & Prener, 1954) and the term 'murdochite-type structure' was introduced and is still used today (Taguchi *et al.*, 1995).

However, a reinvestigation of the crystal structure of murdochite showed that the structure determined by Christ & Clark (1955) was erroneous (Dubler *et al.*, 1983). It turned out that the mineral murdochite contains considerable quantities of chlorine and bromine, and that the true chemical composition is $\text{Cu}_6\text{PbO}_{8-x}(\text{Cl},\text{Br})_{2x}$, with $x \leq 0.5$ (Dubler *et al.*, 1983). The new structure proposed by Dubler *et al.* (1983; Fig. 2) has the same space-group symmetry as that suggested by Christ & Clark (1955), $Fm\bar{3}m$, and the Pb and Cu ions occupy the same Wyckoff positions in both structures. The difference between the two is in the location of the O atoms, and in the presence or absence of additional Cl and Br. Of course, structure determinations based on film methods, such as that by Christ & Clark (1955), are rather insensitive to the distribution of O atoms, especially as in murdochite the scattering is dominated by the heavy atoms. The cation coordination polyhedra in the structure proposed by Dubler *et al.* (1983) are PbO_8 cubes and elongated CuO_4X_2 polyhedra rather than PbO_6 and CuO_6 octahedra, as suggested by Christ & Clark (1955). The struc-

ture as determined by Dubler *et al.* (1983) can be described as being composed of isolated PbO_8 cubes, which are arranged on a f.c.c. (face-centered cubic) lattice. All cube edges are linked by planar CuO_4 groups, whereby cavities in between the cubes are formed (Fig. 2). According to Dubler *et al.* (1983) these cavities are partly filled by the halogen ions.

The studies mentioned above leave several questions unanswered. Firstly, the formula of murdochite has not yet been rigorously established, as from the available data it is unclear if halogen-free Cu_6PbO_8 crystallizes in the structure suggested by Dubler *et al.* (1983) or whether the presence of Cl and/or Br is required to stabilize the structure. Attempts by Dubler *et al.* (1983) to synthesize halogen-free Cu_6PbO_8 failed and they could not reproduce the results of Winchell & Wenden (1969), who claimed to have obtained murdochite as a by-product during the synthesis of diaboileite. Secondly, it could be possible that Cu_6PbO_8 is polymorphous and that Christ & Clark (1955) and Dubler *et al.* (1983) determined the structures of two different polymorphs. A transition between the two structures has to be reconstructive and hence a high-pressure or high-temperature polymorph could exist as a metastable phase. Finally, physical properties of murdochite other than the structure and its density have not yet been reported. In the absence of synthetic samples, an elegant approach to clarify the open questions is to utilize first-principles quantum mechanical calculations. These can reliably

predict the relative stability and properties of different polymorphs, and are thus well suited to address the remaining unanswered questions.

It is noteworthy that today numerous compounds besides Mg_6MnO_8 are known which crystallize in the structure described by Christ & Clark (1955). Most of them are halogenides. These are often called 'Suzuki-phases' after Kazuo Suzuki, who described the first example, Na_6CdCl_8 (Suzuki, 1961).

2. Computational details

The quantum mechanical calculations performed here are based on density functional theory (DFT). While DFT itself is exact (Hohenberg & Kohn, 1964), practical calculations require an approximation for the treatment of the exchange and correlation energies. Here we use an approximation which is termed the 'generalized gradient approximation' (GGA; Perdew *et al.*, 1992). Results based on GGA calculations are generally in better agreement with experiment than those obtained with the local density approximation (LDA; Leung *et al.*, 1991; Hammer *et al.*, 1993; Goniakowski *et al.*, 1996; Hamann, 1996).

The DFT calculations were performed with a plane-wave basis set for the charge density and wavefunctions (Payne *et al.*, 1992). This has advantages with respect to the calculation

of forces and stresses compared to other, more complex, basis sets (Singh, 1994). However, as it is impractical to explicitly consider tightly bound core electrons when using a plane-wave basis set, pseudopotentials have to be used which mimic the screening of the Coulomb potential of the nucleus by the core electrons. A number of approaches for the construction of pseudopotentials have been presented in the literature (*e.g.* Bachelet *et al.*, 1982; Kleinman & Bylander, 1982). State-of-the-art are the very efficient 'ultrasoft' pseudopotentials, which require a comparatively small number of plane waves (Vanderbilt, 1990; Kresse & Hafner, 1994). Such ultrasoft pseudopotentials were used here, with a maximum cut-off energy of the plane waves of 380 eV. In addition to the cut-off energy, only one further parameter determines the quality of the calculations, namely the density of points with which the Brillouin zone is sampled. Here we used 10 k -points in the irreducible part of the Brillouin zone, which were chosen according to the Monkhorst–Pack scheme (Monkhorst & Pack, 1976). For the calculations we used academic and commercial versions of the *CASTEP*

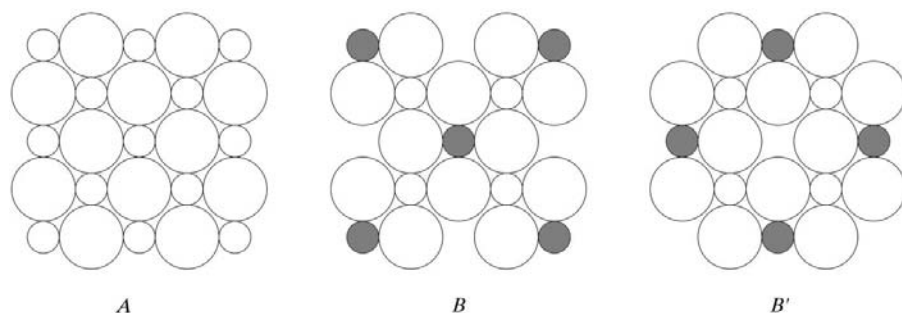


Figure 1

Schematic representation of the structure proposed by Christ & Clark (1955) for Cu_6PbO_8 . Large open circles represent O, small open circles Cu and small filled circles Pb. The structure might be envisaged as being stacked out of layers in the order $ABAB'$.

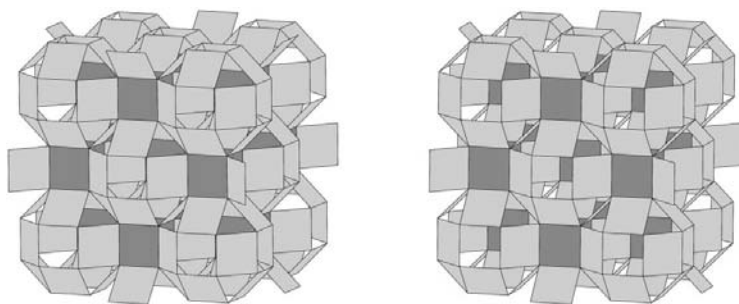


Figure 2

Stereo drawing of the structure of halogen-free murdochite as determined by Dubler *et al.* (1983). Isolated PbO_8 cubes shown in dark grey form an f.c.c. lattice. Planar CuO_4 groups (light grey) share two of their edges with two different PbO_8 cubes. This arrangement leads to the formation of large cavities, which may be occupied by Cl or Br.

program, which has been described elsewhere (Payne *et al.*, 1992; Molecular Simulations, 1998).

3. Results

3.1. Ambient pressure

At ambient pressure the calculations of Cu_6PbO_8 in the structure suggested by Dubler *et al.* (1983) converge with a lattice parameter of $a = 9.314 \text{ \AA}$, corresponding to a volume of $121.7 \text{ cm}^3 \text{ mol}^{-1}$ and a density of 5.9 g cm^{-3} , in good agreement with experimental data (Table 1).¹ The only free internal parameter of the structure proposed by Dubler *et al.* (1983) is the fractional coordinate of the oxygen on Wyckoff position 32(*f*) ($x \ x \ x$). We find $x = 0.145$ and thus bond lengths of 2.337 (Pb—O) and 1.935 Å (Cu—O), again in good agreement with experimental findings.

The results obtained for Cu_6PbO_8 in the structure proposed by Christ & Clark (1955) are markedly different. Here, we find a lattice parameter of $a = 8.623 \text{ Å}$, a volume of $96.5 \text{ cm}^3 \text{ mol}^{-1}$ and a density of 7.4 g cm^{-3} (Table 1). All these data do not match experimental findings, neither those of Dubler *et al.* (1983) nor those of Christ & Clark (1955). The only free internal parameter, the x position of the O2 atom, is 0.252 (in fractional coordinates) and the oxygen is already at room pressure slightly displaced towards the vacancy. The lengths of the Pb—O2 and Cu—O2 bonds are 2.173 and 2.156 Å , respectively; the length of the Cu—O1 bond is within the accuracy of calculation equal to that of the Cu—O2 bond.

A comparison of the computed total energies shows that at ambient pressure the atomic arrangement determined by Dubler *et al.* (1983) is more stable by 433 kJ mol^{-1} than a hypothetical polymorph with the structure proposed by Christ & Clark (1955). It is well known that calculations such as those presented here give binding energies which are accurate to within a few kJ mol^{-1} (Kong *et al.*, 1990; Ortiz, 1992; Perdew *et al.*, 1992). Furthermore, for calculations of similar structures, the errors inherent in DFT calculations tend to cancel out. Thus, the accuracy of the calculated energy difference between the two polymorphs is certainly better than 1%. An overview of the results obtained at ambient pressure and a comparison with the experimental data of Dubler *et al.* (1983) is given in Table 1.

3.2. Pressure dependence and phase transition

We calculated the structural parameters of halogen-free murdochite at 11 pressures between -3 and 59 GPa (Fig. 3). From these data we derived a compressibility of $K_0 = 126.5$ (3) GPa , with a pressure derivative $K_1 = 4.67$ (2), by fitting a third-order Birch–Murnaghan EOS (Birch, 1978)

$$E(V) = c_1 + (9c_2V_0K_0/4)\left\{\left((K_1/4) - 1\right)\left[(V_0/V)^2 + 3(V_0/V)^{2/3} - 3(V_0/V)^{4/3}\right] + 1/2(V_0/V)^{4/3} - (V_0/V)^{2/3}\right\}. \quad (1)$$

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: SH0137). Services for accessing these data are described at the back of the journal.

Here, c_1 is an arbitrary offset and c_2 a conversion factor. If E is measured in eV, K_0 in GPa and V_0 in Å^3 , c_2 has the numerical value $1/160.2192$. V_0 is the volume per formula unit at zero pressure, K_0 the adiabatic bulk modulus at zero pressure, and $K_1 = dK_0/dp$, where p denotes the pressure. Similarly, we derived $K_0 = 145$ (5) GPa and $K_1 = 4.4$ (2) from 16 high-pressure calculations between -4 and 73 GPa for Cu_6PbO_8 in the structure proposed by Christ & Clark (1955; Fig. 3).

As the calculations presented here correspond to a temperature of 0 K , the enthalpy $H = E + pV$ determines the relative stabilities of the two polymorphs under the influence of external pressure. We find that on increasing pressure the Cu_6PbO_8 polymorph proposed by Christ & Clark (1955) becomes the stable phase. The phase transition pressure is 17.8 (2) GPa (Fig. 4). This pressure might alternatively be determined from a common tangent construction, which gives a transition pressure of 18.0 (4) GPa (Fig. 3). The phase transition is accompanied by discontinuities in the molar volume and in the density with $\Delta V = 22.2 \text{ cm}^3 \text{ mol}^{-1}$ (-20%) and $\Delta\rho = 1.7 \text{ g cm}^{-3}$ ($+25\%$).

The value of each internal parameter of both structures depends linearly on the lattice parameter. In the case of the low-pressure phase, *i.e.* the polymorph whose structure was determined by Dubler *et al.* (1983), the relationship is $x = 0.1548$ (1) $- 0.0011$ (1) a . In the case of the hypothetical high-pressure phase, which has the structure proposed by Christ & Clark (1955), it is $x = 0.4336$ (16) $- 0.0211$ (2) a . As in both cases the fractional coordinate varies only slightly over the investigated lattice parameter range, in practice all cation–

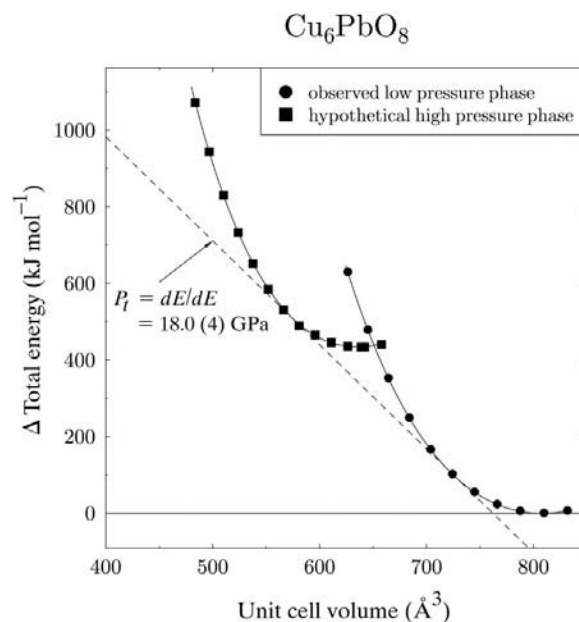


Figure 3

The computed volume-dependence of the total energy of Cu_6PbO_8 relative to the total energy of halogen-free murdochite at 0 GPa ($E_{\text{murd}, 0 \text{ GPa}} = -1285085.3 \text{ kJ mol}^{-1}$). The solid lines connecting the data points are fits with third-order Birch–Murnaghan equations-of-state. The dashed line is a graphically constructed common tangent to both data sets. Its slope equals the transition pressure.

Table 1

Comparison of experimental room-temperature data of Dubler *et al.* (1983) with calculated data from this study.

Additionally, predictions for the hypothetical high-pressure polymorph with the structure suggested by Christ & Clark (1955) at ambient pressure are shown.

	Murdochite			High-pressure polymorph
	Dubler <i>et al.</i> (1983)	This study	Difference (%)	This study
a (Å)	9.224 (2)	9314	+1.0	8.623
V (cm ³ mol ⁻¹)	118.2	121.7	+3.0	96.5
ρ (g cm ⁻³)	6.1	5.9	-3.3	7.4
$d_{\text{Cu-O}}$ (Å)	1.921 (1)	1.935	+0.7	2.156
$d_{\text{Pb-O}}$ (Å)	2.283 (1)	2.337	+2.4	2.173

oxygen bond lengths decrease linearly with decreasing lattice parameter.

4. Discussion

The results presented above clearly indicate that the structure suggested by Dubler *et al.* (1983) is stable without partial filling of the cavities with halogens and that it is significantly more stable at ambient pressure than the structure proposed by Christ & Clark (1955). The computed lattice parameter, density and bond lengths are in good agreement with experimental findings (Table 1). In contrast, the lattice parameter of a hypothetical Cu₆PbO₈ polymorph with the structure assumed by Christ & Clark (1955) would be much smaller at ambient pressure than the value observed for murdochite (Christ & Clark, 1955; Dubler *et al.*, 1983). This implies that the partial filling of the empty cavities in Cu₆PbO₈ with Cl/Br according to Cu₆PbO₈ + $x/2$ (Cl/Br)₂ = Cu₆PbO_{8-x}(Cl/Br)_x + $x/4$ O₂ has only a minor effect on the lattice constant.

The bond lengths predicted for murdochite at ambient pressure are in good agreement with crystal chemical experience. The Cu–O bond length calculated with the effective ionic radii for planar coordination given by Shannon (1976) is 1.96 Å, while we find 1.935 Å. Similarly, for Pb–O in cubic coordination one expects 2.36 Å and the computations yield 2.337 Å. Even for the hypothetical high-pressure phase, the bond lengths at 0 GPa are consistent with the ionic radii of Shannon (1976), which give for a Cu–O bond in octahedral coordination 2.19 Å. This agrees well with the 2.156 Å we predict. For Pb–O in octahedral coordination the figures are 2.175 and 2.173 Å, respectively. Hence, the structure proposed by Christ & Clark (1955) is less stable not because the arrangement of atoms requires an unfavorable or unusual bonding, but rather because the octahedral coordination of both lead and copper leads to a very dense arrangement, which is unfavorable at low pressures.

It is crystal-chemically interesting that already at ambient pressure the O₂ in the hypothetical high-pressure polymorph with the structure proposed by Christ & Clark (1955) is slightly displaced towards the vacancy. Naively one would expect a displacement towards the divalent cation, as is observed in Suzuki phases such as Na₆CdCl₈ (Chall *et al.*,

2000). Obviously, the Pb atoms have such large ‘radii’ that the O₂ is already pushed into the vacancy at ambient pressure.

The calculated compressibilities of halogen-free murdochite and its predicted high-pressure polymorph are of the order of magnitude typical for oxides with small cations (Knittle, 1995). The bulk modulus of the denser high-pressure phase is 15% larger than that of murdochite, which is also comparable to findings for other pairs of polymorphs.

Increasing pressure leads to a relative stabilization of the much denser hypothetical structure and at a pressure of ~18 GPa it becomes more stable. The large predicted discontinuities in the molar volume and the density of -20% and +25%, respectively, are not uncommon for high-pressure phase transitions involving a change in coordination number. In the case of the phase transition of SiO₂ from coesite to stishovite, which occurs at room temperature at ~8 GPa, the relative change in volume is over -30% and in density +40% (Hemley *et al.*, 1994). Similarly, in the case of the phase transition of ZnO from the wurtzite into the rocksalt structure at 8.6 GPa and 0 K, Jaffe & Hess (1993) found $\Delta V = -20\%$ and $\Delta\rho = +25\%$ with Hartree–Fock calculations.

As the proposed phase transition is reconstructive, it is conceivable that Cu₆PbO₈ in the hypothetical structure proposed by Christ & Clark (1955) might exist metastably at ambient pressure and that in fact Christ & Clark (1955) determined the structure of this polymorph. However, this hypothesis can be excluded, as Christ & Clark (1955) report a

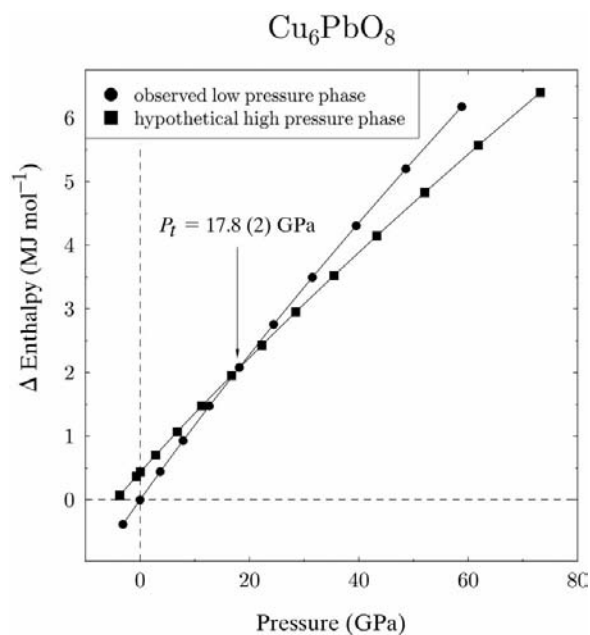


Figure 4

The computed pressure-dependence of the enthalpy of Cu₆PbO₈ relative to the enthalpy of halogen-free murdochite at 0 GPa ($H_{\text{murd}, 0 \text{ GPa}} = -1285.0853 \text{ MJ mol}^{-1}$). The solid lines connecting the data points are guides to the eye. Their crossing point has been determined graphically.

lattice parameter of 9.210 (2) Å. This is 7% larger than the ambient-pressure lattice parameter predicted in this study, well outside the range of uncertainty of the methods employed here.

This then implies that the term ‘murchisonite-type structure’ should be avoided. Murchisonite does not crystallize in this structure, except for the high-pressure modification of murchisonite predicted here. Instead we suggest to employ alternatively the well established term ‘Suzuki structure’, as compounds such as $\text{Na}_6\text{Cd}\square\text{Cl}_8$ do actually exist with the structure proposed by Christ & Clark (1955).

In summary, we have answered the questions posed in the introduction as follows: pure halogen-free Cu_6PbO_8 is stable and crystallizes in the same crystal structure as the mineral murchisonite. Furthermore, Cu_6PbO_8 is polymorphous. However, the phase transition occurs only at high pressures. The predicted bulk moduli, their pressure dependences and the predicted transition pressure could be investigated by conventional high-pressure X-ray diffraction using diamond anvil cells, provided a sample material could be synthesized. Therefore, we hope that this computational study might stimulate further experimental research on Cu_6PbO_8 .

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