

Calculations of structural and electronic properties of manganese dioxide

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Abstract. Manganese dioxide is an important material for electrochemical applications; including serving as a cathode material in Li-ion batteries. It is a non-stoichiometric compound that exists in many crystalline forms, such as α -, β -, γ -, δ -types. The γ -MnO₂ has a complex structure, composed of intergrowths of pyrolusite and ramsdellite structures, twinned ramsdellite, grain boundaries, dislocations and point defects (vacancies and impurities). Experimental methods were used to characterise electrolytic manganese dioxide materials and there has been no efficient method to characterize their structures and thereby no means of relating their atomic scale arrangement with their behaviour in batteries. We investigate structural and electronic properties of pyrolusite and ramsdellite polymorphs of manganese dioxide, using the density functional theory where pseudopotential plane wave methods are invoked. In particular, the equations of states are determined and bulk moduli predicted. The partial density of states and charge deformations of pyrolusite and ramsdellite, provide information on their nature of bonding at different pressures.

1. Introduction

A considerable amount of work has been done on manganese dioxide since its introduction as a depolarising agent. Among the numerous metal oxides that have the required properties for use in energy storage devices, MnO₂ is most promising. Electrolytic Manganese Dioxide (EMD) is not expensive and has the ability to maintain high discharge rates, a good performance over a wide temperature range and a long storage life. Consequently, EMD is the most widely used cathode material for alkaline batteries, secondary lithium batteries and recently has found application in lithium-air batteries [1-3]. EMD has always been known to be an intergrowth of pyrolusite and ramsdellite structure. The afore-mentioned crystalline polymorphs of manganese dioxide possess intimately related structure due to the similarity of their MnO₆ frameworks. Pyrolusite may be described as infinite single chains of edge sharing octahedral, which are connected by corners to the other single chains whereas ramsdellite structure contains double chains [4].

The structural and electrochemical properties of manganese dioxide have been reported widely for several years [5, 6]. Previously, XRD patterns were used to give a comprehensive description of EMD structure in terms of intergrowth of pyrolusite and ramsdellite domains and microtwinning [7-10]. Structural changes upon proton intercalation and heat treatment were studied using in situ neutron powder diffraction [11]. However, an extensive review by Chabre and Pannetier [6] has pointed out a need for alternate methods to check and complement diffraction techniques.

Different computer simulation techniques have been used successfully to study a wide variety of MnO₂ properties. In particular, different defect models of EMD were generated and relaxed using

classical lattice energy minimisation [12]. First principles calculations were carried out on proton intercalation in the pyrolusite and ramsdellite polymorphs of MnO_2 [13], and to understand the effect of other point defects on the structural stability [14]. The atomistic simulation technique was used to study structures for pyrolusite and ramsdellite systems [15]. Simulated amorphisation and recrystallisation technique was used to study nano and bulk MnO_2 [16, 17]. Defect rich microstructures whose structural properties compare reasonably with experimental results were generated. However, owing to complexity of the material, experimental work on electronic properties was never reported. Density functional theory, DFT [18] has provided a convenient first principle framework for studying the structural and electronic properties of a wide range of materials.

In this study we present a theoretical study of electronic and structural properties of pyrolusite and ramsdellite polymorphs of MnO_2 in order to understand its structural complexity. The total geometry optimisation is performed using the computer code CASTEP. Calculated structural (lattice parameters and equation of states) and electronic properties (density of states, charge differences and deformations) calculated are presented. The charge deformations give information on the type of bonding in the systems.

2. Methodology

Planewave pseudopotential (PWP) method is used to perform calculations on pyrolusite and ramsdellite structures. Within the density functional theory, Local Spin Density Approximation (LSDA) simulation was performed. In PWP plane wave basis set is used for expanding electronic states. In order to reduce the number of plane waves required, chemically inactive core electrons are effectively replaced with ultrasoft pseudopotentials, which were taken from the CASTEP database in this work. There are two parameters that affect the accuracy of the calculations, that is, kinetic energy cut-off, which determines the number of plane waves in the expansion and the k-points used for the Brillouin zone integration. Therefore it is very important to ensure that appropriate energy cut-off and k-points used. The lattice parameters, pressure-volume (PV) dependences of the equation of states (EOS) and the bond lengths for pyrolusite and ramsdellite structures are predicted using the PWP method. Geometry optimisation was achieved by varying the hydrostatic pressure and allowing the lattice to relax using Broyden-Fletcher-Goldfarb-Shano (BFGS) minimisation method. Electronic minimisation was performed using band-by-band conjugate gradient (CG) method.

Energy cut-off is the important parameter in PWP calculations because it determines the number of plane waves required in a calculation. Calculations on different values of energy cut-off were performed until a constant minimum energy is obtained, thus the energy becomes stable and the cut-off energy that corresponds to the minimum total energy is recorded. For pyrolusite and ramsdellite, the energy cut-off used is 600eV. The cut-off energies correspond to Fast Fourier Transform (FFT) grid of $30 \times 30 \times 20$ and $74 \times 52 \times 24$ for pyrolusite and ramsdellite respectively. The total number of plane waves used is 1000 for pyrolusite and 2000 for ramsdellite. Pulay correction on forces was included to compensate the energy cut-off. In all optimisations, the tolerance in total energy and pressure change before self-consistency was 2×10^{-5} eV/atom and 0.1GPa respectively. The RMS tolerance for the atoms displacement was restricted to 0.001Å. Within the LSDA, spin of 6 and 12 were used for pyrolusite and ramsdellite respectively.

3. Results and Discussions

Structural and electronic properties of pyrolusite and ramsdellite are presented in this section. The effect of pressure on the systems is discussed in particular, the equation of states, density of states and charge differences, at pressures ranging from -20GPa to 50GPa, were determined.

3.1. Structural properties

Prediction of the geometric and electronic structures of a solid requires a calculation of the total energy of the system and subsequent minimisation of that energy with respect to nuclear coordinates and electronic coordinates.

3.1.1. *Structural parameters.* The results of the equilibrium lattice parameters and bond lengths for pyrolusite are listed in table 1. The results are based on LSDA forms of exchange correlation interaction using the computer code CASTEP. The lattice parameters and bond-lengths were calculated for each hydrostatic pressure. The application of pressure to the system shows a relative shortening of the bond lengths. At a low pressure, 0GPa, the bond lengths are in reasonable agreement with the experimental values. As expected, they are reduced significantly at higher pressure. The Mn-Mn bond length decreases more rapidly than the one for O-O interactions. The lattice parameters are reduced as the pressure is increased. The total energy minimisation gives lattice parameters results which are in good experimental as they are listed in table 1.

Table 1. Calculated pyrolusite structural properties compared with experimental values.

	a (Å)	c (Å)	V (Å ³)	Mn-O (Å)	O-O (Å)	B (GPa)
Calculated	4.47	3.00	61.54	1.95	2.76	156.9
Experimental [19]	4.41	2.86	55.81	1.87	2.68	

Prediction of the volume of a system indicates how accurate the system is being modelled. The structural properties of ramsdellite structure at 0GPa are listed in table 2 showing the lattice parameters, bond lengths and bulk modulus. The results were obtained using the LSDA. The approximation underestimated the total volume of the system. The system relaxes more along the b-direction. The atoms are moving out along this direction. The results are within the acceptable margins of error. The Mn-O and O-O bond lengths are well reproduced.

Table 2. Structural parameters for ramsdellite, calculated and experimental.

	a (Å)	b (Å)	c (Å)	V (Å ³)	Mn-O (Å)	O-O (Å)	B (GPa)
Calculated	9.473	4.055	2.876	111.62	1.884	1.881	73.07
Experimental [20]	9.355	4.479	2.854	119.55			
Experimental [21]	9.37	4.467	2.850	119.29	1.915	1.903	

3.1.2. *Pyrolusite equation of state.* The equation of state (EOS) results are used to predict bulk moduli of the two polymorphs. Compressibility of the systems is illustrated by the change in relative volume with pressure. The bulk modulus of the system is defined by equation $\bar{B} = -V_0 \frac{\partial P}{\partial V}$. The bulk modulus was deduced from figure 1 by fitting the Murnaghan's third order equation of state and it was found to be 156.9GPa for pyrolusite and 73.1GPa for ramsdellite. Presently there are no experimental results to compare with. The bulk modulus deduced from the graph of lattice parameter against V/V_0 and is lower than that predicted for the pyrolusite structure.

3.2. Electronic Properties

The electronic properties of a material help in understanding the classification of the material under three main categories, i.e., metals, semiconductors and insulators. The type of material is determined by the size and existence of the energy gap between the highest occupied orbitals (conduction band) and the lowest unoccupied orbitals (valence band). In metals, the occupied and unoccupied orbitals overlap, therefore no gap between the bands is noted. In semiconductors and insulators the gap is present which tends to be larger for insulators.

3.2.1. *Charge density difference.* Charge density differences (crystal minus superposition of atoms) are of immense interest since they inform us on the nature of bonding between the oxygen and manganese atoms and also play a major role in determining the electronic properties of MnO₂. Some features of

charge density differences can be linked to the information obtained from the total and partial density of states. The charge density differences for pyrolusite are shown in figure 1 for the pressure at 0GPa and 50GPa. The magnitude of charge is shown by different colours with the red and blue indicating gain and loss respectively. It is noted that four lobes of Mn have depleted charge (blue). Two lobes with charge gain are seen around Mn. Since charge differences show how charge is shared among the atoms during bonding, it is evident that charge is transferred from O^{2-} to Mn^{4+} . At 0GPa, relatively more covalent bond is noted between oxygen and manganese with the polarization of the oxygen electron cloud towards manganese. At 50GPa the Mn-O bonds appear to be ionic, with the oxygen charge more spherically concentrated on the oxygen 2p lobes.

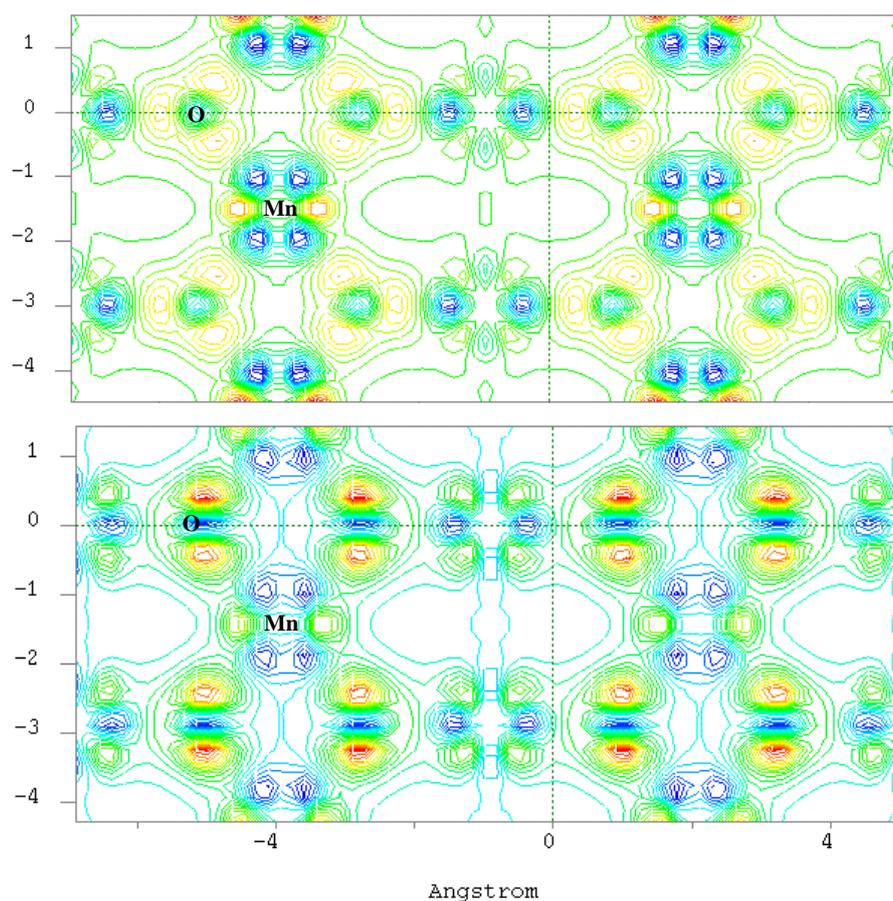


Figure 1. Charge density difference for pyrolusite at 0GPa (top) and 50GPa (bottom).

The charge density differences for ramsdellite are shown in figure 2 for 0GPa pressure. The charge differences appear to be a mixture of covalent and ionic bonding between manganese and oxygen. The directionality of the oxygen charge distribution indicates the presence of covalent bonding. It is noted that at both pressures there is ionicity between manganese and oxygen atoms.

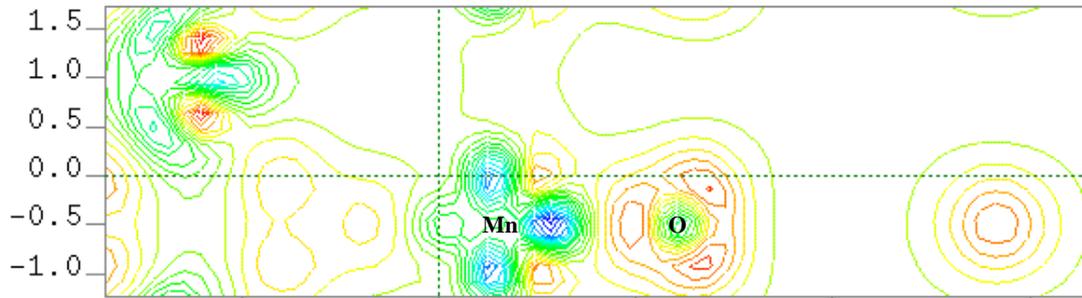


Figure 2: Charge density difference for ramsdellite at 0GPa.

3.2.2. *Density of states.* Figures 3 depicts the partial density of states (PDOS) for pyrolusite structures. PDOS gives the atomic contributions of a material. Considering the projections over atomic orbitals, the sequence of peaks appearing from the valence band to the conduction band can be interpreted as discussed below.

For pyrolusite, the first double peak in the valence band corresponds to 5d(Mn) and also the first maximum peak in the conduction band (figure 4 top). The first peak at approximately at -14eV in figures 3 bottom is 2s(O). This is followed by a broad peak that corresponds to 2p(O). There is small contribution of s and p orbitals for manganese in the valence band and a strong contribution in the conduction band. The valence band is dominated by the 5d contribution. Oxygen shows no d-orbital contribution, it is dominated by s and p orbitals in the low energy band and a small contribution of p orbital in the high energy band. The pyrolusite system appears to be metallic at 0GPa and becomes an insulator at 50GPa. The band gap at 50GPa is estimated as 2.8 eV. This behaviour tends to agree with the observation noted on the charge density differences where the covalent and ionic bondings are dominant at 0 and 50GPa respectively.

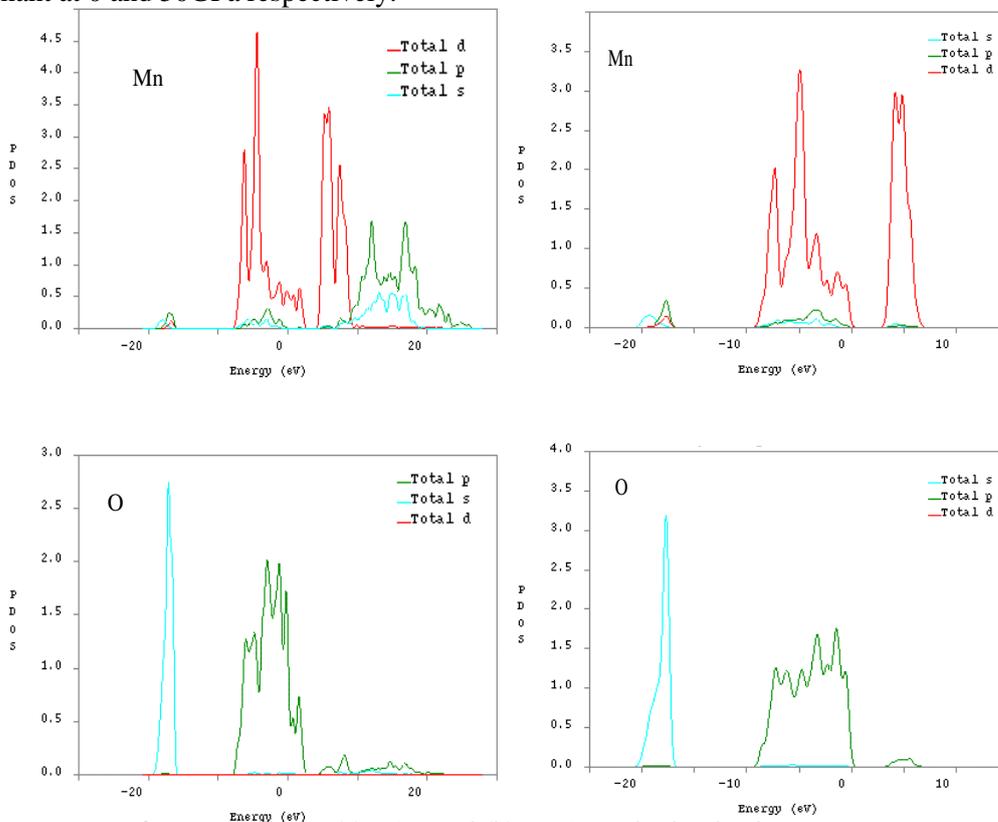


Figure 3. PDOS for pyrolusite at (a) 0GPa and (b) 50 GPa obtained using LSDA, Mn contributions at the top and O at the bottom.

For ramsdellite, at approximately -17eV, we note a small contribution of all the orbitals. The Mn 5d orbital dominates the contribution in both the valence and conduction bands. The PDOS results reveals peaks of non-bonding O s orbital at energy of -17eV. It is followed by a wide band with low contribution from the p orbital. The low contribution of O p orbital is noted at the top of the valence band and lastly a very small contribution in the conduction band. The calculations predict that the system is an insulator at both 0GPa and 50GPa. Application of pressure to the system results in no closure of the gap. However, it reduces the band gap from 4.8 eV at 0 GPa to 2.5 eV at 50GPa. Hence ramsdellite remains in an insulating state.

4. Conclusion

The density functional theory technique has been applied successfully to the study of structural and electronic properties of pyrolusite and ramsdellite systems. We have determined a suitable energy cut-off, which is 600 eV, for both systems and the k-points. We have also deduced the bulk moduli from P versus V/V₀ curve. The equation of state has been calculated for each of the systems involved, pyrolusite and ramsdellite, including the structure optimisation and derivation of the bond lengths changes with pressure up to 50GPa. The charge density difference and the partial density of states predicts the nature of bonding in both compounds. There no literature results to compare with, hence these are the predictions.

References

- [1] Urfer A, Lawrance G A and Swinkels D A J 1997 *J. Appl. Electrochem.* **27** 667
- [2] Kordesch K V and Dekker M 1994 Batteries, Marcel Dekker, New York 1974 1, chapter 2
- [3] Kordesch K V and Welssenbacher M 1994 *J. Power Sources* **51** 61
- [4] MacLean L A H and Tye F L 1996 *J. Solid St. Chem.* **123** 0163
- [5] Thackeray M M, Rossouw M H, Cummow R J, Liles D C, Pearce K, De Kock A, David W I T and Hull S 1993 *Electrochimica Acta* **38** 1250
- [6] Chabre Y and Pannetier J 1995 *Prog. Solid State Chem.* **23** 1
- [7] Ripert M, Pannetier J, Charbe Y and Poinsignon C 1991 *Mat. Res. Soc. Symp. Proceed. Series* **210** 359
- [8] Pannetier J 1992 *Progress in Battery and Battery Materials, IBA Sydney Meeting* **11** 52
- [9] Pannetier J 1993 *Proceedings of 8th IBA Meeting, Brussels, Progress in Batteries and Battery Materials* **13** 132, ITE-JEC Press Inc. 1994
- [10] De Wolff P M 1959 *Acta Cryst.* **12** 341
- [11] Shilling O and Dahn J R 1998 *J. Appl. Cryst.* **31** 398
- [12] Hill J-R, Freeman C M and Rossouw M H 2004 *J. Solid State Chem.* **177** 165
- [13] Balachandran D, Morgan D and Ceder G 2002 *J. Solid State Chem.* **166** 91
- [14] Balachandran D, Morgan D, Ceder G and van de Walle A 2003 *J. Solid State Chem.* **173** 462
- [15] Maphanga R R, Parker S C and Ngoepe P E 2009 *Surf. Sci.* **603** 3184
- [16] Sayle T X T, Catlow C R A, Maphanga R R, Ngoepe P E and Sayle D C 2005 *J. Am. Chem. Soc.* **127** 12828
- [17] Sayle T X T, Catlow C R A, Maphanga R R, Ngoepe P E and Sayle D C 2006 *J. Cryst. Growth* **294** 118
- [18] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
- [19] Brenet J and Acad C R 1950 *Sci. Paris* **230** 1360
- [20] Abou-El-Sherbini K S 2002 *J. Solid State Chem.* **166** 371
- [21] Kondrusev L D and Zaslavskij A I 1951 *Izr. Akad. Nauk SSSR Ser. Fiz* **15** 179